ANNUAL TECHNICAL REPORT
1969 - 1970

MATERIALS RESEARCH
IN THE

CENTER FOR
MATERIALS SCIENCE AND ENGINEERING

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

submitted to the
ADVANCED RESEARCH PROJECTS AGENCY
CONTRACTS SD-90; DAHC15 67 C 0222

DECEMBER 1, 1970

229

ANNUAL TECHNICAL REPORT
on
MATERIALS RESEARCH
September 16, 1969 to September 15, 1970

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by the
CENTER FOR MATERIALS SCIENCE AND ENGINEERING
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Mass.

December 1, 1970

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INTRODUCTION

A summary of the activities in research and graduate education at the Center for Materials Science and Engineering at the Massachusetts Institute of Technology during the academic year September 16, 1969 - September 15, 1970 is presented in this Annual Technical Report.

The Center was established in 1961 to promote and support interdisciplinary research and education in materials through contractural support, in part, from the Advanced Research Projects Agency of the Department of Defense. The extent of support provided by the Services and other government agencies is indicated in the report.

The Center has a physical existence in the Interdisciplinary Laboratory Building, dedicated in 1965 as the Vannevar Bush Building, which houses professors, post-doctoral research staff, graduate students, support groups, and the central facilities and services necessary for balanced materials research. The Center provides an administrative staff to oversee the physical facility and to maintain budgetary control of the contract funds.

The Center also makes possible person-to-person contact, person-to-facility exposure, and an atmosphere conducive to thinking, doing, questioning, and achieving which is both stimulating and energizing. Much of this is provided through course work, small research conferences, colloquia, visitors from the U. S. and abroad, from study groups on selected topics and by hosting engineering and scientific conventions.

The professors, post-doctoral research staff, and the graduate students are appointed by the academic departments through the usual academic processes. Their association with the Center can be through occupation of office and laboratory space, use of the extensive central facilities, participation in the series of colloquia, and through financial support in terms of salaries, materials, or equipment.

The existence of many individual research programs, derived through the initiative of the individual professor and made possible through the excellence and performance of his graduate students, post-doctoral, and technical support staff, is not new in the academic research environment. The existence of a wide range of shared central facilities, equipped with the most modern equipment, supplied with materials which may be standard or highly specialized, and managed by interested faculty or staff members, provides the Center with a kind of stimulus new to university research. In addition, the training of graduate students to operate such facilities, the

discussions concerning the potentials or limitations of facilities and processes, and the immediate guidance from experts instill confidence in the students and provide the desired interdisciplinary input to his program.

The research programs of the Center are administered by a Director with the Advice of the Committee on the Center. The Committee consists of the Deans of the Schools of Science and of Engineering, the Heads of all the Departments of Science and Engineering, and ex-officio the Provost of M.I.T., to whom the Director reports in keeping with the interdepartmental character of the Center.

Newly organized interdisciplinary ventures are planned on the basis of interdisciplinary study groups; the recommendations of these study groups provide the interested faculty with a detailed view of overall activity in a given field and provide a basis for planning new research.

The research programs are reported at length in the pages following. The sponsorship of the research is given for each project. Personnel who have received direct salary support in any degree from ARPA Contract SD-90 are indicated by *. The many others who receive benefits from the central facilities and other services provided by ARPA are not identified.

The graduate education program is implicit in the listings of the graduate students involved in each research project, their degrees, their theses and publications, and the destinations to which they are carrying out their advanced education in the specific disciplines of their department combined with the experience gained through participation in the work of the Center.

Nicholas J. Grant, Director
Center for Materials Science and Engineering

COLLOQUIA SERIES

We would like to thank Professors B. L. Averbach, H. E. Stanley, and S. Moss, for ably performing as the organizing commitee for the Fall and Spring terms, 1969-1970 colloquia.

We are also grateful to the following speakers for their contribution to the 1969-1970 series.

Professor H. E. Stanley, Dept. of Physics, MIT
"The Science and Lore of Phase Transitions and Critical Phenomena"

Professor Carl W. Garland, Dept. of Chemistry, MIT
"Critical Phenomena from) Hz to 20 GHz; Dynamical Studies of Order-Disorder Transitions"

Professor Leo P. Kadanoff, Dept. of Physics, Brown University
"Dynamic Critical Phenomena: Theory of Coupling Among Modes"

Dr. Boris A. Strukov, Moscow State University, Visiting Scientist, MIT
"Specific Heat and Ultrasonic Attenuation Anomalies Near the Curie Temperature of Uniaxial Ferroelectrics"

Professor S. C. Moss, Dept. of Metallurgy and Materials Science, MIT
"The Effects of Long Range Interaction Potentials on Critical Scattering of X-rays and Electrons from Alloys"

Dr. Jens Als-Nielsen, Danish Atomic Energy Research Establishment, Visiting Scientist, Brookhaven National Laboratory
" The Order-Disorder Transition in Beta Brass"

Professor Takeo Izuyama, Dept. of Physics, Tokyo University, Visiting Professor of Physics, Northeastern University
"Itinerant Ferromagnetism"

Professor Leonard W. Gruenberg, Dept. of Electrical Engineering, MIT
"The Resistive Transition in Superconductors"

Professor George E. Benedek, Dept. of Physics, MIT
"Theory of the Transparency of the Eye"

Professor Richard C. Lord, Dept. of Chemistry, MIT
"Laser-Raman Studies of Biomolecules"

Professor Robert Meyer, Division of Engineering and Applied Physics, Harvard University
"Microstructure of Nematic Liquid Crystals"

Dr. Michael Hart, Lecturer in Physics, Bristol University
(on leave at the NASA Electronics Center)
"X-ray Interferometry"

Dr. Robert F. Rushmer, Director, Bioengineering Program
University of Washington
"Biomaterials: An Essential Ingredient for Bioengineering"

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Metallurgy and Materials Science

Materials Engineering

I. SOLID STATE MOLECULAR THEORY GROUP

Faculty:

J. C. Slater, Institute Professor, Emeritus, Physics
G. F. Koster, Professor, Physics
P. D. DeCicco, Assistant Professor, Physics
R. Gilmore, Assistant Professor, Physics
K. H. Johnson, Assistant Professor, Metallurgy and Materials Science

Graduate Students:

H. Brandi, Physics
D. Klingspon, Physics

Support Staff:

Vera Sarantakis, Materials Science Center, Secretary

Sponsorship:

Advanced Research Projects Agency, SD-90 DSR 75106
National Science Foundation, NSF-GP-3241, DSR 70607

Research Report

In line with our previous ARPA Reports, we indicate the fields of interest of the members of the group by listing the titles of the contributions to our Progress Reports issued during the year, namely Semi-Annual Progress Reports Nos. 72 and 73 issued on January 15, 1970 and July 15, 1970 respectively.

Contributions to Semi-Annual Progress Reports Nos. 72 and 73

P. D. Decicco, Compton Scattering of X-rays in Solids II, 72
P. D. Decicco, Computational Aspects of the APW Method, 73
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R. Gilmore, Spectrum of Casimir Invariants for the Simple Classical Lie Algebras, 72
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K. H. Johnson and J. W. D. Connolly, The Relativistic Energy B and Struc-

ture of Gold, 72

K. H. Johnson and F. C. Smith Jr., SCF Molecular-Orbital Studies of the Sulfate Ion by the Scattered-Wave Model, 73

Publications

P. D. DeCicco, Compton Scattering of X-rays from Crystals in the One-electron Model, Intern. J. Quantum Chem. (to be published)

P. D. DeCicco, Energy Bands by the LCAO-Cellular Method, Proceedings of the IBM Conference on Computational Methods in Band Theory (to be published)

K. H. Johnson and J. W. D. Connolly, The Electronic Structures of Cesium Chloride Type Intermetallic Compounds, Intern. J. Quantum Chem. 3S, 813 (1970)

J. W. D. Connolly and K. H. Johnson, The Electronic Densities of States and Optical Properties of CsCl Type Intermetallic Compounds, Proc. 3rd IMR Symposium, Electronic Density of States, Nat. Bur. Stand. (U.S.), Spec. Publ. 323 (1970)

K. H. Johnson and F. C. Smith Jr., Cluster-Wave Approach to the Electronic Structures of Complex Molecules and Solids, Phys. Rev. Letters 24, 139 (1970)

K. H. Johnson, Generalized Scattered-Wave Approach to Molecular-Orbital Theory, Intern. J. Quantum Chem. (to be published)

K. H. Johnson and F. C. Smith Jr., Bands, Bonds and Boundaries, Proceedings of the IBM Conference on Computational Methods in Band Theory (to be published)

II. NONEQUILIBRIUM QUANTUM STATISTICAL MECHANICS

Faculty:

M. O. Scully, Associate Professor, Physics

Research Staff:

H. Auvermann, Visiting Scientist
C. Chang, Research Associate
F. Hopf, Visiting Scientist
D. Hyman, Instructor in Physics
D. M. Kim, Instructor in Physics
T. Nee, Visiting Scientist (University of Arizona)
D. Rogovin, Research Associate
P. Sastry, Visiting Scientist (Tufts University)
R. Shaw, Instructor in Physics

Graduate Students:

I. Asher, Research Assistant, Physics
J. Goldstein, Research Assistant, Physics
R. Lang, Research Assistant, Physics
P. Lee, Research Assistant, Physics
D. Limbert, Research Assistant, Physics
K. Whitney, Research Assistant, Physics

Support Staff:

Vera Sarantakis, Secretary, Center for Materials Science and Engineering

Sponsorship:

Advanced Research Projects Agency SD-90, DSR 75105
Air Force Office of Scientific Research

Degrees Granted:

P. Lee, Ph. D., Physics
D. Limbert, M. S., Physics
K. Whitney, Ph. D., Physics

Introduction:

Our research has continued into several areas of quantum statistics involving quantum mechanical coherence, such as quantum optics, coherent pulse propagation, superconductivity and cooperative phenomena. During the past year much of this work was carried out at the University of Arizona. Their hospitality was very much enjoyed and appreciated.

The following are connected with these efforts:

i) The principal investigator was awarded the Adolph Lomb medal for contributions to quantum optics and is currently a John Simon Guggenheim fellow.

ii) Dr. P. Lee was appointed to the Gibbs Instructorship at Yale University.

iii) Other members of the group received permanent positions in industrial laboratories and at the Universities of Rice and Arizona.

iv) Invited papers and talks were presented at several meetings, colloquia, and summer schools.

Research Report

1.0 Build-Up of Laser Oscillations from Quantum Noise

Build-up of laser oscillation is expressed in terms of the probabilities $p_n(t)$ that there are n photons in the laser cavity. These probabilities obey a coupled set of difference-differential equations of motion. The method and results of numerical integration of these equations are obtained for the initial condition that no photons exist (radiation field vacuum). Corresponding equations of motion for the moments of the photon distribution are derived, and their time dependences found.

2.0 Quantum Theory of Mode Locking

Previous theories of laser radiation have described the electromagnetic field in terms of a discrete set of quasi-modes (Fox and Li modes) of the laser cavity. Each mode was assumed to have a finite quality factor Q. In steady state (when gain due to lasing atoms cancels the losses), the theory predicts a delta function line shape. In the present work the semiclassical laser theory is generalized for a maser with a cavity having a semi-transparent wall as one of the mirrors so that there are many modes corresponding to each Fox-Li type mode. It is demonstrated that the coupled multimode equations can be reduced to an equation of form found in the usual quasi-mode theory.

3.0 The Laser as a Phase Transition

An interesting comparison may be made between second-order phase transitions, such as the order-disorder transitions of ferromagnetic and ferroelectric materials or the vapor-liquid transition of a pure fluid, and the laser near threshold. It is well known, for instance, that the state of a laser changes abruptly upon passing through the threshold point. Furthermore, the laser-field fluctuations and the decay times associated with these fluctuations are much larger in the vicinity of threshold. In the present work we have demonstrated that the laser- threshold behavior is very analogous to a second-order phase transition.

4.0 A Theory of Time Dependent Phenomena in Ferromagnetism

Using methods developed in connection with analysis of lasers, a microscopic calculation of time-dependent effects in a ferromagnet is carried out. The equation of motion of the density operator of the ferromagnet coupled to a thermal reservoir is converted to a C-number equation for a quasi-probability distribution function for the magnetization. The molecular field equation of state is obtained as the steady state solution of the equation of motion for the average magnetization. The steady state probability distribution of the magnetization is found as a function of temperature and reduces to that suggested by Landau near the Curie temperature.

5.0 Zero π Pulse Propagation

The propagation behavior of nontrivial zero-π pulses ($\int_{-\infty}^{\infty}\mathcal{E}(t,z)dt = 0$, $\int_{-\infty}^{\infty}\mathcal{E}^2(t,z)dt>0$) in attenuating media is examined. It is found that under appropriate conditions zero-π pulses exhibit anomalously low absorption which is a direct consequence of atomic coherence. Specific analytical results valid for an unbroadened medium are presented while the corresponding solutions for an inhomogeneously broadened resonance are calculated numerically. These two results are consistent in the limit of $T_2^* \to \infty$. Furthermore, the influences of T_2, T_2^*, and level degeneracy on the characteristics of propagation are determined. Finally, the behavior of more general zero-π pulses is studied. The criteria for the production of zero-π pulses are qualitatively established by numerical methods and the influence of the relative phase of pulse pairs on propagation is examined. The latter indicates a method for the measurement of relative pulse phase.

6.0 Coherence and Noise in Josephson Radiation

We consider the problem of a Josephson junction interacting with a quantized electromagnetic field contained in microwave cavity. Inasmuch as the cavity has a quality factor Q and an external current J flows in and out of the junction, this is a problem in non-equilibrium statistical mechanics. We use a technique that eliminates adiabatically the radiation field directly from the total density matrix equation of motion. The resulting equation for the reduced density matrix is found to have a simple physical interpretation. The spectrum of the voltage fluctuations and the line-width of the emitted radiation are then calculated for the case when the resonance cavity is at absolute zero.

7.0 Effects of Blackbody Radiation in Josephson Radiation

The effects of blackbody radiation inside the resonance cavity of a Josephson junction on the voltage fluctuations and the radiation line-width are considered. Using the technique of the associated classical representation for the density operator equation, we adiabatically eliminate the radiation field variable and obtain the equation of motion for the reduced density matrix. The voltage fluctuation spectrum and the line-width of the emitted radiation are then calculated. As a result of a fully quantum mechanical treatment we find that the current-voltage characteristics are slightly modified by the presence of the blackbody photons. A physical argument for this effect is given and possible experimental observation of this effect discussed.

8.0 Density Matrix, Green's Function, and Quantum Noise Operator Technique in Quantum Optics

A review article of density matrix, Green's function, and quantum noise operator theoretical techniques and ideas that have been prominent in the development of quantum optical theory is nearing completion. A simple, exactly solvable model involving a linear radiation mode interaction is used to compare the three theoretical approaches. This linear model describes a many-body atomic-radiation field interaction for which the atomic system is passive and reservior-like and for which the radiation mode evolves under a Markovian dynamics. Emphasis is given to the dual nature and similarity of these three theoretical descriptions: that is, to the ways in which equivalent statements are made about the statistical state radiation mode in the presence of the reservoir interaction. The comparison of the different ways in

which the three theories produce this information is crucial to an appreciation of how they complement each other in their description of more complicated systems. In each theoretical case, calculations of spectral and Hauvury Brown-Twiss mode correlation functions are carried out to demonstrate the equivalence of the theories and to offer comparison of the three methods by which these correlation functions can be calculated. Next, a discussion is given of the corresponding density matrix, Green' s function, and quantum noise operator reservoir theory of a two-level atom. The radiation mode, reservoir model is extended and it is shown that a radiation mode that has been thermalized by a reservoir of atoms has the reciprocal effect of acting as a reservoir for an atom, bringing the atom to thermal equilibrium with its environment. At first, the quantum noise operator theory of the radiation mode is used to derive a corresponding quantum noise operator theory for the two-level atom. The results of this noise operator theory are then rederived using density matrix theory, again to demonstrate equivalence of the theoretical approaches. Finally, some comments about the future developments of optical theory are made.

9.0 A Correlation Function Calculation of the Spectral Profile of Josephson Radiation about its Central Frequency

A paper in which a Green' s function or forward-and-backward-time formalism calculation of the output spectral profile of Josephson radiation is carried out, is also being prepared for publication. The calculation is based on a model of the Josephson junction electron-pair dynamics which assumes that the electron-pairs tunnel across the junction and radiate photons that have an energy equal to the potential energy of the pairs prior to tunneling. The radiation acquires its spectral properties because the electron-pair current oscillations are modulated by charge fluctuations and the pair radiation superposes over a background of thermal radiation. The calculation has three parts to it. The first part presents a simple argument which demonstrates that the effect of charge fluctuations is to damp the electron-pair current oscillation and that the damping constant is simply related to a charge fluctuation correlation function. In part two, equations that relate the time evolution of the charge fluctuation correlation function to current-current correlation functions are derived. From these equations, which describe in general a non-Markovian time evolution of the charge fluctuations, a Markovian determination of the charge fluctuation correlation function is made. The result is in agreement with previous quantum noise operator and density matrix calculations of the same correlation function. Finally, in the

third part, a calculation, based on a linearized damped current, damped modes interaction, of the mode spectral correlation function is carried out. The calculation shows that while the Josephson radiation linewidth is determined by charge fluctuations, there is no significant frequency pulling of the radiation from the value $2eV/\hbar$, where V is the potential difference across the junction.

10.0 Time Dependent Superconductivity

The behavior of superconductors under general non-equilibrium conditions has been the subject of much study since 1966. However, little progress has been made in this area due to the difficulty of doing many-body calculations for systems in the non-equilibrium state. In response to this, two separate avenues of research have been pursued.

In one, a general formalism has been developed to deal with situations in which the system is subject to external fields which can vary with arbitrary frequency. Using the Gorkov equations, formal solutions just off the BCS state have been obtained. For large perturbations a diagrammatic formalism has also been developed. In particular, we are now studying the effect of weak, but high-frequency radiation on the gap and the way that the gap behaves when this field is turned off.

Second, a Schrödinger-like wave equation has been obtained for $\Delta(r,t)$. This approach leads in a natural way to Josephson tunneling and the formalism obtained enables one to investigate the basic response times of Josephson junctions when subjected to rf or magnetic fields.

Publications:

P. Lee and M. Scully, "Josephson Radiation I: General Theory" Submitted to Phys. Rev.

P. Lee and M. Scully, "Josephson Radiation II: Effects of Blackbody Radiation" Submitted to Phys. Rev.

P. Lee and M. Scully, "Noise in Tunnel Junctions" Proceedings of Precisions Measurements Conference. To be published.

P. Lee, "Effect of Noise on Current Voltage Characteristic of a Josephson Junction", J. Appl. Phys. To be published.

D. Hyman, "On Evaporation from He II", Phys. Letters. To be published.

V. DeGiorgio and M. Scully, "An Analogy Between Laser Threshold Region and a Second Order Phase Transition", Phys. Rev. Oct. 1970.

T. Arrechi and D. Kim, "Collective Effects in Superradiance", Phys. Rev.

To be published.

C. S. Chang and P. Stehle, "Q. E. D. Theory of Atoms Interacting with High Intensity Radiation Fields," Phys. Rev. To be published.

C. S. Chang and P. Stehle, "Resonant Interaction Between Two Neutral Atoms" Phys. Rev. To be published.

F. Hopf and M. Scully, "Transient-Pulse Behavior and Self-Induced Transparency", Phys. Rev. 1, 50 (1970).

F. Hopf, "Multiple Pulse Propagation and Self-Induced Transparency."

F. Hopf, G. Lamb, C. Rhodes and M. Scully, "On Zero Pi Pulses", Phys. Rev. Nov. 1970.

M. Sargent, M. Scully and W. Lamb, "Build-Up of Laser Oscillations from Quantum Noise", Applied Optics. Fall 1970.

M. Scully and S. Jacobs, "Coherence - A Sticky Subject" (an invited lead article) Applied Optics.

M. Sargent and M. Scully, "Theory of Laser Operation", Laser Handbook. Ed. by T. Arrechi.

III. ATOMIC RESONANCE AND SCATTERING

Faculty:

D. Kleppner, Associate Professor, Physics

D. E. Pritchard, Assistant Professor, Physics

Research Staff:

* Dr. M. T. Myint, D.S.R. Research Staff, Center for Materials Science and Engineering

Graduate Students:

F. Y. Chu, Research Assistant, Physics

E. Mattison, Research Assistant, Physics

William Phillips, National Science Foundation Fellow

F. G. Walther, Research Assistant, Physics

Support Staff:

Malinda Rieck, Secretary, Center for terials Science and Engineering

Personnel who have left:

F. P. Winkler (now at Middlebury College)

Degrees Granted:

F. P. Winkler, Ph.D. (Harvard University) June, 1970

Sponsorship:

Research Laboratory of Electronics, supported by Joint Services Electronics Program under contract DA 28-043-AMC-02536(E), DSR 72252

Bureau of Standards, NBS 0830, DSR 72547

National Science Foundation, GP 13633, DSR 71799

* Advanced Research Projects Agency, SD-90, DSR 72207

1.0 Superconducting Particle Counter

Personnel: Professor D. Kleppner; Dr. M. Than Myint

Sponsorship: ARPA

Research Report:

We are investigating the feasibility of a thin film superconducting device intended to respond to energy pulses of 1 eV or less. A sensitivity of 1 eV would permit it to count hydrogen atoms by detecting their reaction energy when they undergo chemical combination on the detector's surface. Conceivably, the sensitivity will be 0.1 eV or less, in which case the device could operate as an infrared photon counter. This would provide an increase in sensitivity of many orders of magnitude over present infrared detectors. Applications for such a device would be numerous.

We have successfully detected alpha particles and electrons with energies down to 300 eV, using tin films. Spurious counts are negligible and the efficiency appears to be high. Our current efforts are directed at detecting optical photons and hydrogen atoms.

2.0 Research with the High-Field Hydrogen Maser

Personnel: Professor D. Kleppner; William Phillips, Frederick G. Walther, P. Frank Winkler

Sponsorship: Joint Services Electronic Program, Bureau of Standards

Research Report:

We have completed a detailed analysis of experimental corrections and uncertainties for our determination of the magnetic moment of the proton. The result, which has been submitted for inclusion in the evaluation of the table of fundamental constants, is $-g_j(H)/g_p(H) = 658.2107061(65)$. Work is underway to determine the effect of binding on the magnetic moment of the electron by comparing the electron moment in hydrogen and deuterium. This is of particular interest because it is sensitive to corrections of order $\alpha^2 m/M$, and possibly $\alpha^3 m/M$, for which there has recently been theoretical and experimental controversy.

3.0 Spin-Exchange Scattering

Personnel: Professors D. Kleppner and D. E. Pritchard; Frank Chu

Sponsorship: Research Laboratory of Electronics

Research Report:

We have extended the work on scattering of polarized alkali beams in which the polarization of the scattered beam is measured. Measurements made this year include several alkali-rare gas systems and the alkali-molecule systems K-N_2, K-NO, and K-O_2.

The analysis of the new scattering data requires more detailed models than were used in the analysis of earlier data on alkali-alkali scattering, and we have begun work on methods which permit more

accurate determination of the potential from the scattering cross section.

We are currently trying to measure the magnetic resonance spectrum of weakly bound alkali-rare gas molecules. The scattering data shows that these molecules should be bound by roughly 1/40 eV (cf. 1-2 eV for "normal" molecules), which means that they will dissociate at room temperatures. We hope to produce them in an adiabatically expanding gas jet and study them before they collide with anything warm.

Theses:

F. P. Winkler, "A Precise Determination of the Proton Magnetic Moment," Ph. D., Department of Physics (Harvard University) June 1970.

Publications:

D. Kleppner, "The Magnetic Moment of the Proton-and All That," Proceedings of the 1st International Conference on Fundamental Constants, U. S. Bureau of Standards, August 1970.

D. Kleppner, "New Molecules for Molecular Beams," Proceedings of Second International Conference on Atomic Physics, Oxford University, July 1970.

D. E. Pritchard, Phys. Rev. A1, 1120, 1970, "Interpretation of Interference Structure in Elastic Scattering Using the Semiclassical Action".

IV. NEUTRON DIFFRACTION AND NEUTRON PHYSICS STUDIES

Faculty:

C. G. Shull, Professor, Physics

Research Staff:

Dr. C. Stassis, DSR Staff, Physics

Dr. J. A. Oberteuffer, DSR Staff, Physics

Graduate Students:

C. Stassis, Research Assistant (until January 1970), Physics

C. deLatour, Research Assistant, Physics

D. Frank, Research Assistant, Physics

Support Staff:

Susan Leonard, Secretary, Physics

Vera Sarantakis, Secretary, Physics

A. d' Addario, Project Technician, Physics

Degrees Granted:

C. Stassis, PhD, Physics, January 1970

C. deLatour, MS, Physics, September 1970

Sponsorship:

U. S. Atomic Energy Commission, AT-30-1-3031, DSR 72051

National Science Foundation, GP-8303, DSR 70981

Research Report

1.0 Study of the Kondo Effect in Cu-Fe Alloys

Personnel: C. Stassis and C. G. Shull
Sponsorship: U. S. Atomic Energy Commission

Polarized neutron diffraction studies have been carried out on crystals of Cu-0.1 % Fe above and below the Kondo ordering temperature while in an externally applied magnetic field of 15 kilo-oersteds. The field induced magnetization at the impurity sites and its modification with the development of

the low temperature spin-compensated state is studied through its effect on the Bragg reflected intensity. The magnetic form factor has been established as being of localized 3d-electron origin and its temperature dependence in the region 25-2.2^{o}K shows a gradual deviation from free spin behaviour with decreasing temperature. The localized susceptibility characteristic of the neutron measurements was found to agree in both absolute magnitude and temperature dependence with the total susceptibility measured by Professor D. Sellmyer on the same crystals. This implies the absence of any large field induced polarization in the spin-compensating conduction electron cloud. The Kondo temperature was found to be about 6^{o}K corresponding to a localized spin fluctuation lifetime of 10^{-12} seconds.

2.0 Diamagnetic Scattering of Slow Neutrons

Personnel: C. Stassis and C. G. Shull
Sponsorship: U. S. Atomic Energy Commission

Preliminary measurements of the field induced diamagnetism in bismuth have been carried out by polarized neutron diffraction. The origin of the anomalously large diamagnetism in bismuth is not understood theoretically and a study of the form factor and magnitude of the diamagnetic scattering may contribute to this understanding. A theoretical study of the diamagnetic form factor and its relation to the charge form factor has been carried out so that it is possible in principal to identify the electron group responsible for the diamagnetism. Present measurements on the (110) reflection with an applied field of 22 kilo-oersteds show agreement with that calculated from the core electrons only. Further measurements at other reflections and with much higher field strength are in progress.

3.0 Pendellosung Fringe Structure in Bragg Reflections from Silicon Crystals

Personnel: C. G. Shull and J. A. Oberteuffer
Sponsorship: U. S. Atomic Energy Commission

Using full spectrum neutron radiation from the M. I. T. Reactor, the Pendellosung fringe pattern within the (111) reflection of silicon has been scanned to high order as a function of neutron wavelength. After applying small corrections for finite slit width and residual curvature of the crystal planes, very excellent consistency has been obtained with five sets of fringe

data using three different crystal slices. The data show unambiguously that the coherent neutron wave front is spherical and not planar in its passage through the crystal. The fringe patterns are being used to establish the silicon scattering amplitude with very high precision, better than one part in 5000.

4.0 Operation of a Neutron Velocity Selector

Personnel: C. deLatour
Sponsorship: National Science Foundation

A mechanical velocity selector has been constructed and tested for use as a neutron energy filter or as a low resolution spectrometer. It consists of 200 parallel channels which are twisted in helical fashion about the axis of a cylindrical rotor. Its resolution and transmission characteristics have been tested over the wavelength range 3-8 Å and compared with those expected from the design.

Theses:

C. J. Stassis, "Study of Some Aspects of Nagaoka's Quasibound State by Neutron Diffraction", Ph. D., Department of Physics, January 1970.

C. deLatour, "A Study of Neutron Spectra using a Mechanical Velocity Selector", M. S., Department of Physics, September 1970.

Publications:

Y. Ito and C. G. Shull, "Coherent Neutron Scettering by Cobalt with Nuclear Polarization", Phys. Rev. 185, 961 (1969).

C. Stassis and C. G. Shull, "Neutron Diffraction Study of the Kondo Effect in Cu-Fe", J. Appl. Phys. 41, 1146 (1970).

C. Stassis, "Diamagnetic Scattering of Slow Neutrons", Phys. Rev. Letters 24, 1415 (1970).

V. CRITICAL PHENOMENA IN FLUIDS AND SOLIDS.
DIFFUSION COEFFICIENTS OF BIOLOGICAL MACROMOLECULES.
DYNAMICAL PROPERTIES OF GASES NEAR EQUILIBRIUM.

Faculty:

* G. B. Benedek, Professor, Physics

Research Staff:

V. Degiorgio, NATO Fellow

* J. B. Lastovka, D.S.R. Staff, Center for Materials Science and Engineering

D. Schaefer, National Science Foundation and Sloan Foundation Fellow

J. Zollweg, National Science Foundation Fellow and D.S.R. Staff (CMSE)

Graduate Students:

D. Cannell, N.S.F. Fellow

* N. Clark, Research Assistant, Physics

* S. B. Dubin, Research Assistant, Physics

J. H. Lunacek, Research Assistant, Physics

G. Feke, Research Assistant, Physics

* G. Phillies, National Science Foundation Fellow

I. Smith, Fannie and John Hertz Fellow

G. Hawkins, K. T. Compton Fellow

Support Staff:

* Malinda Rieck, Secretary, Center for Materials Science and Engineering

Degrees Granted and Posts Taken:

D. Cannell (Ph.D. Physics, August 1970)
to Department of Physics, University of California at Santa Barbara, Assistant Professor of Physics

* J. H. Lunacek (Ph.D. Physics, August 1970)
to Department of Physics, University of California at Santa Barbara, Postdoctoral Fellow in Physics

N. Clark (Ph.D. Physics, May 1970)
to Division of Engineering and Applied Physics, Harvard University, Postdoctoral Fellow

* S. B. Dubin (Ph. D. Physics, January 1970)
  to Department of Physics, California State College in Fullerton, Assistant Professor of Physics
* J. B. Lastovka, Ph. D.
  to Research Staff, Bell Telephone Laboratories, Murray Hill, New Jersey

John Zollweg, Department of Chemistry, University of Maine, Assistant Professor of Chemistry

Dale Schaefer, Staff Member, I. B. M. Research Laboratories, Yorktown Heights, New York

V. Degiorgio, Department of Physics, University of Milan, Italy

Sponsorship:

* **Advanced Research Projects Agency, SD-90, DSR 75102**

Sloan Fund for Basic Research in the Physical Sciences

National Science Foundation, Fellowship Program

U. S. Army Research Office-Durham, DAH CO4-69-C-0034, DSR 71437

CRITICAL PHENOMENA IN SOLIDS AND FLUIDS

1.0 Phonon Lifetimes and Phonon Velocities in Ammonium Chloride

Personnel: G. Benedek; J. H. Lunacek

Sponsorship: Army Research Office-Durham

Status:

Mr. Lunacek has completed a study of the temperature dependence of the attenuation and velocity of hypersonic sound waves as a function of direction of propagation using Brillouin scattering spectroscopy. He has discovered that a relaxation of the sound velocity occurs and that the relaxation rate is dependent upon the direction of propagation of the sound wave. The temperature dependence of the relaxation rate is similar to that observed in ultrasonic attenuation measurements but differs from it by a factor of four. The experimental results and analyses are being prepared for publication by Dr. Lunacek who has received his Ph. D. degree.

2.0 Measurements of the Thermal Diffusivity and Equation of State of Sulfur Hexafluoride Near its Critical Point

Personnel: G. B. Benedek; J. B. Lastovka, G. Feke

Sponsorship: Advanced Research Project Agency SD-90

Status:

Dr. Lastovka has measured the thermal diffusivity along the coexistence curve of SF_6 to within one degree of the critical point. He has also determined the shape of the critical isotherm, and the compressibility and the density along the coexistence curve. These results and their important implications for the mode-mode coupling theories for the divergence of the transport properties of fluids have been written up and will be published in the Proceedings of the Conference on Critical Phenomena sponsored by the Battelle Institute. Mr. Gilbert Feke is continuing the measurements into the region within one degree of the critical point where the divergence of the transport coefficients will be strongest.

3.0 Viscosity and Surface Tension at the Gas-Liquid Interface in Xenon Near its Critical Point

Personnel: G. B. Benedek; J. Zollweg and G. Hawkins

Sponsorship: Advanced Research Project Agency and National Science Foundation

Status:

Dr. Zollweg and Mr. Hawkins have succeeded in measuring the viscosity and surface tension of xenon along the coexistence curve from $(T - T_c) = 4.5^{\circ}C$ to $(T - T_c) = .110\ ^{\circ}C$. The surface tension varies like $(T - T_c)^{\mu}$ over two orders of magnitude in the variable $(T - T_c)$. The viscosity varies only very slowly. Data analysis and data taking is still underway to establish very accurately the value of the exponent μ. Theories of critical phenomena connect this exponent with the characteristic exponent for the temperature dependence of the correlation range. The present data is valuable in obtaining information on the manner in which the long range correlation grows in the fluid near the critical point.

4.0 Hypersonic Sound Velocity and Attenuation Near the Critical Point of Xenon

Personnel: G. B. Benedek and D. Cannell

Sponsorship: Advanced Research Project Agency and National Science Foundation

Status:

Dr. Cannell has succeeded in deducing the temperature dependence of the relaxing bulk viscosity along the critical isochore in xenon. He has also succeeded in deducing from his spectral information the temperature dependence of the correlation range along the critical isochore. This represents the first determination of the correlation range along this

important thermodynamic path and enables an accurate test of theoretical predictions for the connection between the thermal diffusivity and the correlation range. The results of this experiment have been written up in the form of a Physical Review Letter which is in press for the October 26 issue.

DIFFUSION CONSTANTS OF BIOLOGICAL MACROMOLECULES

5.0 Measurement of Molecular Weight of Bacteriophage Viruses

Personnel: G. Benedek and S. B. Dubin

Sponsorship: Advanced Research Projects Agency and Army Research Office-Durham

Status:

Our determination of the molecular weight of the viruses T4, T5 and T7 has been written up in the form of an article which has been accepted for publication in the Journal of Molecular Biology.

6.0 Denaturation of Lysozyme and Determination of Rotational Diffusion Constant of Natural Lysozyme

Personnel: G. B. Benedek; S. B. Dubin, N. Clark

Sponsorship: Advanced Research Projects Agency, Army Research Office-Durham

Status:

We have successfully completed our measurements of the diffusion constant of lysozyme as a function of its denaturation by guanidine hydrochloride. We have found that the effective size of the enzyme doubles after its passage through the denaturation transition. By studying the spectrum of the depolarized light scattered by natural lysozyme we have successfully measured its rotational diffusion constant. By combining this with translational diffusion constant measurements we have been able to show that the shape of this molecule in solution is much the same as that deduced from the x-ray diffraction patterns of crystallized lysozyme.

7.0 Hydrodynamic Properties of Tobacco Mosaic Virus

Personnel: G. B. Benedek; D. Schaefer

Sponsorship: Advanced Research Projects Agency, Sloan Fund for Research in Physical Sciences

Status:

The rotational, average translational and anisotropic translational diffusion has been studied by analyzing the non-Lorentzian spectra of

tobacco mosaic virus. We find $\bar{D}$ the average translational diffusion constant is $(0.4 \pm 0.02) \times 10^{-7} cm^2/sec$. The rotational diffusion constant is $420 sec^{-1}$ and $D_{\parallel} - D_{\perp}$ the difference between the diffusion coefficients for motion along the rod and perpendicular to the rod is effectively zero. The theoretical analysis of the line shape and the experimental data is written up and will be submitted for publication.

DYNAMICAL PROPERTIES OF GASES NEAR EQUILIBRIUM

8.0 Spectrum of Light Scattered from Pure Xenon Gas and Mixtures of Xenon and Helium

Personnel: G. B. Benedek; N. Clark

Sponsorship: Advanced Research Projects Agency, Army Research Office-Durham

Status:

Mr. Clark has completed this thesis work and has been awarded the Ph. D. His experiment showed that at low enough densities that the most accurate solution now available for the Boltzmann equation can provide an accurate prediction for the shape of the spectrum of the light scattered from pure xenon and xenon helium mixtures over a wide range of densities. This work will be prepared for publication.

Theses:

D. Cannell, "Brillouin Scattering in Xenon Near the Critical Point," August 1970, Ph. D. Thesis M. I. T.

J. H. Lunacek "Measurements of the Sound Velocity and Attenuation in Ammonium Chloride by Brillouin Scattering," August 1970, Ph. D. Thesis M. I. T.

S. B. Dubin, "Quasielastic Light Scattering from Macromolecules," January 1970, Ph. D. Thesis M. I. T.

N. Clark, "Inelastic Light Scattering from Thermal Fluctuations in Gases," May 1970, Ph. D. Thesis M. I. T.

Publications:

M. Giglio and G. B. Benedek, "Angular Distribution of the Intensity of Light Scattered from Xenon Near its Critical Point," Phys. Rev. Letters 23, 1145-1149 (1969).

Noel Clark, J. H. Lunacek and G. B. Benedek, "Observation of Brownian Movement Using Light Scattering," Am. J. Phys. 38, 575-585 (1970).

G. B. Benedek, "Divergence of Transport Coefficients in Fluids from Measurements of the Spectrum of Light Scattered Near the Critical Point," Proceedings of XIV International Solvay Conference in Chemistry, Ed. by R. Defay, John Wiley, London (1970).

T. J. Greytak, R. L. St. Peters and G. B. Benedek, "Brillouin Scattering Measurements of the Velocity and Attenuation of High Frequency Sound Waves in Superfluid Helium," Optics Communications Vol. 1, p. 412-416 (1970).

D. S. Cannell and G. B. Benedek, "Brillouin Scattering in Xenon Near its Critical Point," Phys. Rev. Letters, Vol. 25,October 26, 1970.

VI. EXPERIMENTAL STUDIES OF CRITICAL PHENOMENA AND ORDER-DISORDER PHASE TRANSITIONS

Faculty:

* J. D. Litster, Assistant Professor, Physics

Graduate Students:

* D. D. Berkner, Research Assistant, Physics
  T. R. Steger, N. D. E. A. Fellow, Physics
  T. W. Stinson, III, National Science Foundation Fellow, Physics

Support Staff:

* Malinda Rieck, Secretary, Center for Materials Science and Engineering

Sponsorship:

* Advanced Projects Research Agency, SD-90, DSR 75101

Research Reports

1.0 Magneto Optical Studies of the Critical Point

Personnel: J. D. Litster, D. D. Berkner, T. R. Steger

Object:

To use the rotation of the plane of polarization (Faraday Effect) of light transmitted by magnetic solids to determine the temperature dependence of the susceptibility and the field dependence of the magnetization near the critical point of magnetic materials.

Research Report:

We have analyzed our measurements of $CrBr_3$ to obtain several mathematical representations for the equation of state of this material near the critical point. A very successful approach was the parametric representation developed in collaboration with Dr. Peter Schofield (Visiting Professor of Physics from U. K. A. E. A. Harwell). The resulting equation of state is determined (apart from scale factors) by two critical exponents. As a result the entire equation of state may be determined by measurements along two paths in the H-T plane (or P-T plane for fluids). The equation applied equally well to pure fluids in the critical region. It is mathematically simple and easily used for engineering thermodynamic

calculations in the critical region. A preliminary account of this work was published in Phys. Rev. Letters 23, 1098 (1969). A full account of the parametric equation of state and the experimental work on $CrBr_3$ will appear in the December 1970 issue of Physical Review B.

We are continuing experimental work on the properties of magnetic materials in the critical region. Measurements are being made on yttrium iron garnet (YIG) by the Faraday rotation technique to determine the equation of state of this ferrimagnet. The same techniques are also being applied to europium sulfide, which should approach closely the ideal Heisenberg ferromagnet.

2.0 Phase Transitions in Liquid Crystals

Personnel: J. D. Litster, T. W. Stinson

Object:

To study the order-disorder transition in liquid crystals. These studies will elucidate the role of symmetry in order-disorder transitions and provide a basic understanding necessary to the design of optical devices using liquid crystals.

Research Report:

We have been using optical methods to study the phase transition of the nematic liquid crystal p methoxy benzylidene p-n butylaniline (MBBA). The disordered phase has the same properties as an isotropic liquid. In the ordered phase the centers of mass of the anisotropic MBBA molecules are randomly distributed as in an isotropic liquid, but there is a long range parallel alignment of the molecular axes which results in an optically anisotropic liquid. The anisotropy in the dielectric constant provides a direct measure of the order in the liquid, and this may ideally be studied by optical methods.

In the isotropic phase of MBBA we have accurately measured the order induced by a magnetic field (magnetic birefringence), and the intensity and spectrum of light scattered by thermal fluctuations in the order parameter. We observed a divergence of the magnetic birefringence, a divergence in the intensity of the scattered light, and a critical slowing of the fluctuations. These are all phenomena usually observed in the vicinity of a second order phase transition, although the nematic-isotropic transition in MBBA is first order. Our measurements may be quantitatively interpreted using a mean field model; this model also indicates the transition is first order because of the quadrupolar symmetry of the ordered phase.

We have also observed a departure from the mean field model very close to the phase transition; this results from the critically diverging fluctuations as the phase transition is approached. We are continuing to investigate this and other features of the nematic-isotropic transition and will extend our studies to include smectic and cholesteric liquid crystals. We anticipate our studies will elucidate the basic properties of this interesting and potentially useful class of materials.

Publications:

J. T. Ho and J. D. Litster, "Divergences of the Magnetic Properties of $CrBr_3$", J. Appl. Phys. 40, 1270 (1969).

J. T. Ho and J. D. Litster, "Magnetic Equation of State of $CrBr_3$ Near the Critical Point", Phys. Rev. Letters 22, 603 (1969).

P. Schofield, J. D. Litster, and J. T. Ho, "Correlation Between Critical Coefficients and Critical Exponents", Phys. Rev. Letters 23, 1098 (1969).

J. T. Ho and J. D. Litster, "Faraday Rotation Near the Ferromagnetic Critical Temperature of $CrBr_3$", Phys. Rev. B. (to be published Dec. 1970).

J. D. Litster and T. W. Stinson III, "Critical Slowing of Fluctuations in a Nematic Liquid Crystal", J. Appl. Phys. 41, 996 (1970).

T. W. Stinson, III, and J. D. Litster, "Pre-Transitional Phenomena in the Isotropic Phase of a Nematic Liquid Crystal", Phys. Rev. Letters 25, 503 (1970).

I. Haller and J. D. Litster "Temperature Dependence of Normal Modes in a Nematic Liquid Crystal", Phys. Rev. Letters, to be published.

J. D. Litster, "Critical Points and Almost Critical Points", Int. J. of Magnetism, to be published.

J. D. Litster, "Critical Properties of Ferromagnets and Liquid Crystals", to be published in Critical Phenomena, R. I. Jaffee and R. E. Mills ed. (McGraw Hill).

VII. THE DYNAMICS OF QUANTUM FLUIDS

Faculty:

* **T. J. Greytak, Associate Professor, Physics**

Research Staff:

G. Winterling, Visiting Scientist, Center for Materials Science and Engineering

Graduate Students:

* **R. Benjamin, Research Assistant, Physics**
* **D. Rockwell, Kennecott Copper Corporation Fellow, Physics**

R. Woerner, Graduate Student, Physics

* **J. Yan, Research Assistant, Physics**

Senior Students:

G. Mellman, Mathematics

J. Miller, Physics

Support Staff:

Malinda Rieck, Secretary, Center for Materials Science and Engineering

Sponsorship:

* **Advanced Research Projects Agency, SD-90, DSR 75103**

Research Reports

1.0 Rotons in Liquid Helium

Personnel: T. J. Greytak; J. Yan, R. Woerner

Sponsorship: ARPA

Research Report:

We are using high resolution Raman scattering to probe the elementary excitations in superfluid helium. We have found that pairs of rotons, previously thought to interact only weakly, actually form a bound state. The energy of this state is about $0.4^{\circ}K$ less than the energy of two free rotons, $17.3^{\circ}K$, and the wavefunction for the pair is localized in space. We have also measured the roton line width in the range of temperatures,

1.3 to 2.0°K, where it is determined by roton-roton collisions. We find that the full width at half height, δE, of the energy corresponding to a single roton is given by $\delta E/k = (84 \pm 11)T^{1/2} \exp(-E_0/kT)$ in °K where E_0 is the mean energy of a roton. We are using these measurements to test several theories of the interactions between rotons, and we are extending our experiments to dilute solutions of He^3 in He^4 and to pure He^3.

2.0 Thermodynamic Fluctuations Along The Lambda Line in Liquid Helium

Personnel: T. J. Greytak; G. Winterling

Sponsorship: ARPA

Research Report:

We have used Brillouin scattering to study the velocity and attenuation of thermally driven high frequency first sound in superfluid helium. The experimental apparatus is being rebuilt to allow measurements within 100μ°K of the lambda transition from saturated vapor pressure to the solidification pressure of about 30 atmospheres. As the pressure is increased, second sound contributes to the density fluctuations in the medium and gives rise to an additional Brillouin doublet in the spectrum of the scattered light. We will therefore be able to study the velocity and attenuation of second as well as first sound in the lambda region.

3.0 Concentration Fluctuations and Second Sound Near the Phase Separation Point of He^3 - He^4 Mixtures

Personnel: T. J. Greytak; R. Benjamin, and D. Rockwell

Sponsorship: ARPA

Research Report:

We are preparing to study the behavior of first and second sound and concentration fluctuations near the lambda line and the isotopic phase separation curve in He^3 - He^4 mixtures. An argon ion laser has been modified to operate in a single frequency stabilized mode at a power of over one half watt. A spherical Fabry-Perot spectrometer has been completed whose instrumental line width is 5 MHz. The cryostat for the experiment and its associated He^3 refrigerator have been built and are being tested.

4.0 Dynamics of Polyatomic Gases

Personnel: T. J. Greytak; G. Mellman, J. Miller

Sponsorship: ARPA

Research Report:

We are using Brillouin spectra of polyatomic gases to test various extensions of the Boltzmann equation to molecules with internal degrees of freedom. These experiments yield information on the coupling between internal and translational degrees of freedom during collisions. We are also setting up Raman scattering experiments to investigate the transition from free rotation to angular diffusion as the gas density is increased. These experiments can be used to choose between two theoretical models which predict conflicting results.

Publications:

James Yan and T. J. Greytak, "Determination of Roton Linewidths by Raman Scattering," Bull. Am. Phys. Soc. 15, 59 (1970).

R. L. St. Peters, T. J. Greytak, and G. B. Benedek, Brillouin Scattering Measurements of the Velocity and Attenuation of High Frequency Sound Waves in Superfluid Helium, Optics Communications 1, 412 (1970).

T. J. Greytak and James Yan, "Determination of Roton Linewidths by Raman Scattering," Proceedings of the 12th International Conf. on Low Temperature Physics, in press.

T. J. Greytak, R. Woerner, James Yan, and R. Benjamin, "Experimental Evidence for a Two-Roton Bound State in Superfluid Helium, in preparation.

VIII. COOPERATIVE PHENOMENA, SOLID STATE PHYSICS, STATISTICAL MECHANICS, AND BIOLOGICAL PHYSICS

Faculty:

H. E. Stanley, Assistant Professor, Physics

Research Staff:

M. H. Lee, DSR Staff, Physics

Graduate Students:

C. Gordon, Teaching Assistant, Physics
F. Harbus, NSF Fellow, Physics
J. Herzfeld, Research Assistant, Chemistry
J. A. Janzen, USAF Fellow, Physics
D. Karo, NSF Fellow, Physics
R. A. C. Krasnow, Teaching Assistant, Physics
D. N. Lambeth, Teaching Assistant, Physics
K. Matsuno, Research Assistant, Physics
S. Milošević, Research Assistant, Physics
G. Paul, NSF Fellow, Physics
N. Berker, Senior Student, Physics and Chemistry
H. I. Botman, Senior Student, Physics
M. L. Jennings, Senior Student, Physics
S. H. Kinney, Jr., Senior Student, Physics
C. C. Lo, Senior Student, Physics
R. M. Lucash, Senior Student, Physics
D. L. Njus, Senior Student, Physics
R. Roth, Senior Student, Physics
S. Schwartz, Senior Student, Chemistry
R. Koppel, Senior Student, Physics
A. Jenkins, Senior Student, Physics
R. Hansen, Senior Student, Physics

Support Staff:

Vera Sarantakis, Secretary, Center for Materials Science and Engineering

Personnel who have left:

J. A. Janzen, USAF Fellow, Physics

H. I. Botman, Senior Student, Physics (Now at Harvard University)
M. L. Jennings, Senior Student, Physics (Now at Harvard University)
S. H. Kinney, Jr., Senior Student, Physics (Now at Harvard University)
C. C. Lo, Senior Student, Physics (Now at California Institute of Technology)
R. M. Lucash, Senior Student, Physics (Now at Stanford University)
D. L. Njus, Senior Student, Physics (Now at Harvard University)

Degrees Granted:
J. A. Janzen, S. M., Physics, August, 1970
H. I. Botman, S. B., Physics, June, 1970
M. L. Jennings, S. B., Physics, June, 1970
S. H. Kinney, Jr., S. B., Physics, June, 1970
C. C. Lo, S. B., Physics, June, 1970
R. M. Lucash, S. B., Physics, June, 1970
D. L. Njus, S. B., Physics, June, 1970

Sponsorship:
National Science Foundation, GP-15428, DSR 72407
National Aeronautics and Space Administration, NGR 22-009-483, DSR 72150
Research Corporation, DSR 72015
Advanced Research Projects Agency, SD-90 DSR 72204

Research Report

1.0 Linear Response Theory for Systems Obeying the Master Equation

Personnel: S. Milošević and G. Paul
Sponsorship: Advanced Research Projects Agency and National Science Foundation

We have developed the linear response theory for systems whose time dependence is described by the master equation. The fluctuation-dissipation theorem expressing the linear response of the system in terms of fluctuation properties of the system in equilibrium has been derived. As a special case the time dependent Ising model in interaction with a heat bath, the Glauber model, has been discussed.

2.0 An Argument Supporting the Equivalence of the Scaling Law Hypothesis And the Assumption that Critical Point Exponents Exist

Personnel: H. C. Praddaude; H. E. Stanley
Sponsorship: Advanced Research Projects Agency, Research Corporation, National Science Foundation, National Aeronautics and Space Administration

Considerable attention has focused recently upon predictions which follow when one assumes that certain thermodynamic quantities are homogeneous functions (the "scaling law hypothesis"). Clearly a precise mathematical formulation of a small set of assumptions necessary for the validity of the scaling law hypothesis would be extremely useful. We have considered the consequences of a single, quite plausible assumption which is sufficient to prove the equivalence of the scaling law hypothesis and the existence of critical point exponents for a given thermodynamic potential. We also have studied cases when this assumption may not hold and the possibility of the critical point being an essential singularity.

3.0 The Scaling Law Hypothesis and the Spherical Model of Magnetism

Personnel: S. Milosevic
Sponsorship: Advanced Research Projects Agency

The scaling law or "homogeneous function equation of state" hypothesis has received its strongest support thus far from one particular exactly soluble system, the two-dimensional Ising model. Here we consider a test of the scaling laws by examining their validity for what is probably the only exactly-soluble three-dimensional system, the "spherical model" of a magnet. We find that we can rigorously claculate the spherical model critical point exponents for arbitrary dimensionality d. We thereby discover that the relations among the critical point exponents predicted by the scaling laws are satisfied for $d \leq 4$, but not for $d > 4$, and that the recently-observed formal similarity between the spherical model and the ideal Bose gas is complete in the respective critical regions. Finally, we utilize the exact values of the spherical model critical point exponents to judge the relative validity of those numerical extrapolation procedures which are commonly applied in obtaining critical point predictions for models which cannot be solved exactly, such as the Ising and Heisenberg models. In particular, we study the effect of logarithmic terms - present in some of the spherical model indices - upon the behavior of the high-temperature expansion coefficients with a view toward shedding some light on whether the apparent breakdown of the scaling relation $d\nu = 2 - \alpha$ for the $d = 3$ Ising and Heisenberg models might be due to the presence of logarithmic terms.

4.0 Series Expansions and the Universality Hypothesis

Personnel: H. E. Stanley
Sponsorship: Advanced Research Projects Agency, National Science Foundation, Research Corporation, National Aeronautics and Space Administration

This work consists of two parts. In the first part evidence from high-temperature series expansions is presented which supports the hypothesis that critical point exponents may not depend upon such features of the interaction Hamiltonian as (1) the spin quantum number S, (2) the degree of anisotropy, (3) the non-uniformity of the exchange interaction, and (4) the range of the interaction. In the second part one form of the so-called "universality hypothesis" is stated, and a "universality Hamiltonian" is proposed the study of which is expected (according to the universality hypothesis) to encompass the entire range of critical point exponents for systems with short range interactions. The predictions of this Hamiltonian (which essentially corresponds to a system of D-dimensional spins situated on a d-dimensional lattice) are obtained for all values of the parameters D and d.

5.0 Theorems for Series Expansions for the Generalized Heisenberg Model

Personnel: G. Paul
Sponsorship: Advanced Research Projects Agency

We have proved two identities which are extremely useful in developing high temperature series expansions for the isotropic Heisenberg Hamiltonian of arbitrary spin dimensionality. One identity relates the values associated with diagrams for the spin-spin correlation function to the values associated with diagrams for the free energy. The second identity relates the values associated with different diagrams for the free energy which differ, in the language of graph theory, by the insertion of a vertex of valence two.

The second theorem is particularly useful. To calculate expansion coefficients for the free energy to tenth order for loose-packed lattices 298 topologically different diagrams are required. However, only the values associated with 15 basic diagrams must be calculated directly, the rest being obtained by application of Theorem II.

6.0 A Monotonicity Relation for the Two-Spin Correlation Function

Personnel: S. Milošević
Sponsorship: Advanced Research Projects Agency

We have studied the two-spin correlation function $<\underset{\sim}{S}_i^{(D)} \cdot \underset{\sim}{S}_j^{(D)}>$ for the system described by the classical Heisenberg Hamiltonian $\mathcal{H} = -\Sigma_{i,j} J_{i,j} \underset{\sim}{S}_i^{(D)} \cdot \underset{\sim}{S}_j^{(D)}$, where $J_{i,j}$ is the exchange parameter, while $\underset{\sim}{S}_i^{(D)}$ and $\underset{\sim}{S}_j^{(D)}$ are D-dimensional "classical" spins situated at the ith and jth lattice sites. We conjectured that the inequality $<\underset{\sim}{S}_i^{(D)} \cdot \underset{\sim}{S}_j^{(D)}> \geq <\underset{\sim}{S}_i^{(D+1)} \cdot \underset{\sim}{S}_j^{(D+1)}>$ is very plausible. The plausibility comes from the idea that if we increase the spin dimensionality, then the spins have more space in which to "flop about" and hence they are less well correlated. We have been able to prove exactly this inequality for the one dimensional lattice with the nearest-neighbor interaction. A proof for some other cases is the object of our current investigation.

7.0 Critical Properties Obtained by a Conformal Transformation Method

Personnel: M. H. Lee and H. E. Stanley
Sponsorship: Advanced Research Projects Agency, National Aeronautics and Space Administration , National Science Foundation

Critical properties for all realistic three-dimensional models of magnetism are obtained by series extrapolation methods. Considerable uncertainty exists in the estimated critical values for those cases in which the coefficients of a given series do not behave regularly. We argue that the irregular behavior of many series can be understood in terms of non-physical singularities which lie close to and hence "interfere" with the physical singularity. Moreover, we find that the critical values for these series can be estimated reliably by conformally mapping the nonphysical singularities away from the physical singularity with the result that the "transformed series" behaves in a regular fashion. We can then analyze this transformed series using standard methods.

We have applied this technique to obtain critical properties for the Heisenberg, Ising, and XY Hamiltonians for both cubic and for spinel lattices. One particularly interesting result is that the susceptibility exponent for the $S = \frac{1}{2}$ Heisenberg model on cubic lattices has the value $\gamma = 1.36 \pm 0.04$. This value is somewhat lower than the previously-accepted value $\gamma = 1.43 \pm 0.01$, but it is consistent with the scaling law prediction that $\gamma(S)$ be independent of the spin quantum number S.

8.0 Series Expansions for the Spherical and Ising Models with Large Lattice Dimensionality

Personnel: S. Milošević

Sponsorship: Advanced Research Projects Agency

The spherical model can be regarded either as an exactly-soluble approximation to the Ising model or as a model of isotropically interacting spins in which the spin dimensionality D approaches infinity. We have calculated 80 terms in the high-temperature expansions for the spherical model and compared with predictions which would have been obtained if only ~10 terms were known (as in the case for finite D). We find that the critical point exponents deduced from short series are extremely doubtful when d>3, where d is the lattice dimensionality. In particular, we note that it is quite possible that the mean field exponents are valid for all D if d > 3.

9.0 High Temperature Series Expansions for XY Model

Personnel: M. H. Lee

Sponsorship: Advanced Research Projects Agency

A method is developed for the exact high temperature series expansion of thermodynamic properties of the spin $\frac{1}{2}$ XY model of ferromagnetism or of a quantum lattice gas. Eleven coefficients in the specific heat series for the fcc and bcc lattices and nine coefficients in the series for the fluctuation in the long range order for the fcc, bcc and sc lattices are calculated. From the fluctuation series the critical temperatures $K_c^{-1} \equiv kT_c / J$ are estimated to be 4.520, 2.902, and 2.02 respectively, while the critical index for the square of the fluctuation in the long range order is $\gamma \approx 4/3$. The fourth order fluctuation series yields the estimate $\Delta \approx 5/3$, from which by the scaling hypothesis all other indices are obtained. A further linearity hypothesis leads to predictions for the Heisenberg model indices from the Ising and XY indices.

10.0 A Chain of Classical Heisenberg Ferromagnets and an Alternate Version of Monte Carlo Integration

Personnel: S. Kinney, Jr. and H. E. Stanley

Sponsorship: Research Corporation, National Science Foundation

A variant of the Monte Carlo integration technique was used to study the

static properties of a chain of classical Heisenberg ferromagnets. The technique converged rapidly, regardless of the starting conditions, by varying all the spins simultaneously instead of one selected at random. The values for the energy and r. m. s. magnetization compared well qualitatively with theoretical calculations, but compared poorly quantitatively. The problem areas were very high and very low temperatures.

11.0 Collective Excitation Spectrum in the Critical Region of Second Order Phase Transitions

Personnel: K. Matsuno
Sponsorship: Advanced Research Projects Agency

In the critical region of second order phase transitions, critical fluctuations have been known as collective excitations of the system. Such collective excitations have been observed in magnetic materials and gas-fluid systems by scattering experiments. We have investigated theoretically the spectrum of an excitation which may become dominant in the upper critical region where the temperature T is slightly larger than the critical temperature T_c. We assume a bootstrap-like mechanism of the excitation, namely that an excitation and a quasi bound pair of the two such excitations give the same spectrum. This assumption reflects the fact that interactions between the excitations in the critical region are strong enough to mask the distinction between a single excitation and its possible bound pair. With the aid of the assumption, we can determine the retarded propagator of the excitation.

12.0 Liquid Structure Factor of He^4

Personnel: M. H. Lee
Sponsorship: Advanced Research Projects Agency, National Aeronautics and Space Administration, National Science Foundation

Since the work of Feynman, there have been numerous, but unsuccessful, attempts made at deriving from first principles the liquid structure factor which agrees with the Feynman form for small momenta. In recent years, a considerable advance has been made by the method of Jastrow function in obtaining the low temperature properties of liquid helium. Still the usual form of the Jastrow function does not give the correct liquid structure factor. We have shown that this is an inherent weakness of the function

due to the absence of long-wavelength correlations, and that a more satisfactory wavefunction is a generalized function $\Psi(r_1 r_2 \cdots r_N) = \Phi(r_1 r_2 \cdots r_N) \times \prod_{ij} f(r_{ij})$ where Φ is a single-particle product function which contains the properties of independent particle systems and $\prod f(r_{ij})$ the Jastrow function. An effort is being made to derive the liquid structure factor using the above wave function. The derivation of the correct liquid structure factor from first principles will bring about a much more complete understanding of the ground state of liquid helium.

13.0 Multi-Particle Quasi Bound State near the Superconducting Transition Temperature

Personnel: K. Matsuno
Sponsorship: Advanced Research Projects Agency

As one approaches the critical temperature of a superconductor from above, one finds that the life time of the Cooper pairs diverges. It is well known that this quasi-bound pair or collective excitation can influence transport properties such as electrical conductivity, which are dominated by the relaxation phenomena of the Cooper pairs rather than the single particle excitations. We generalized these results by including not only two-particle but also three-particle and four-particle interactions. Our finite tempera - ture Green' s function calculation predicts that as we decrease the temperature, a charged normal Fermi system becomes unstable due to four-particle bound state formation. Here we assumed that bound states consisting of only two, three, and four particles are allowed.

14.0 Cooperative Phenomena in Nerve Membranes

Personnel: D. L. Njus and H. E. Stanley
Sponsorship: Advanced Research Projects Agency, National Aeronautics and Space Administration , National Science Foundation

Nerve cells are rendered excitable by the dependence of the cell membrane' s ionic conductance on the potential difference across the membrane. Although the empirical relationships between conductance and potential are well defined, the mechanism responsible is unknown. This mechanism has recently been postulated to be a cooperative system of active sites that may be treated by the cooperative techniques developed for ferromagnetic spin theory. We have been investigating the case for cooperative phenomena in

membrane conductance. Since the constituent macromolecules are basically linear chains, we believe that a one-dimensional Ising model is conceptually the most accurate. Because conductance data consists primarily of non-equilibrium measurements, we have been developing a dynamic analysis of the linear Ising model.

15.0 Energetics of the Nerve Membrane During Excitation

Personnel: D. L. Njus
Sponsorship: Advanced Research Projects Agency, Research Corporation

We have used a digital computer to simulate the development of a nerve impulse. This provides a theoretical analysis of the thermodynamic changes occurring in the nerve system that can be compared with experimental measurements. This technique can be used to test the potential validity of various membrane models.

16.0 Theory of Permeability in Biological Membranes

Personnel: M. H. Lee and N. Berker
Sponsorship: Advanced Research Projects Agency, Research Corporation

Recent studies on isotope flow in discontinuous systems show that the nature and interactions of lattice sites may govern transport across thin membranes. Where lattice sites play a dominant role (sites being singly or multiply occupied or vacant by species in question), one can interpret the process in terms of statistical mechanical models.

Under consideration are generalized Ising-lattice gas models. Adsorption-desorption at a lattice site, or, equivalently, occupation-vacancy of a site may be regarded as a kind of spin-flip process, and diffusion in the membrane (transfer and switch between sites) may be regarded as a form of cooperativity. Given the Ising Hamiltonian (in the presence of an external field), we can then attempt to connect various membrane parameters to their magnetic analogues and deduce their numerical values. For very thin membranes, the lattice structure is approximately a two-dimensional net.

Due to a certain intrinsic nature of the Ising Hamiltonian, one cannot directly study nonequilibrium aspects of this problem. However, the transition probability (to which the permeability coefficient is related) and other time-dependent correlations can be calculated using a time-dependent version of the Ising model, the Glauber model.

An alternate but related approach also under consideration is to regard flow through the membrane as a quantum mechanical tunnelling process. This approach should be particularly useful in studying the permeability of self-diffusion in the absence of net flow. In the language of many-body problems, adsorption at a lattice site gives rise to creation of a quasi-particle or a group of quasi-particles. These quasi-particles propagate through the membrane and become annihilated by desorption at another lattice site. The transition probability can be handled by time-dependent perturbation techniques developed by us in connection with many-body problems.

17.0 Experimental Problems in Raman Spectroscopy of Biopolymers

Personnel: M. L. Jennings and A. Mooradian
Sponsorship: Advanced Research Projects Agency and Research Corporation

Raman spectroscopy has flourished in the past few years because of lasers and advances in instrumentation. Although research has centered around the study of solids and simple chemical coumpounds, Raman spectroscopy is a potentially powerful tool for the investigation of biological molecules. Several experimental problems, however, have been encountered. High intensity background flourescence is common in the systems studied. Sample preparation and handling is critical. A summary of these problems and ways to cope with them is offered. Some results of a Raman study of the protein lysozyme are reported.

18.0 Intensity Correlation Measurement of Light Scattered from a Solution of Poly-γ-Benzyl-L-Glutamate in 1, 2 Dichloroethane and Dichloroacetic Acid

Personnel: C. C. Lo and S. H. Chen
Sponsorship: Advanced Research Projects Agency

A conventional digital method of performing the intensity correlation of light scattering from molecular number density fluctuations in a solution is described. This method is used to investigate the dependence of the diffusion constant and solute composition of a solution of helix and coiled forms of poly-γ-benzyl-L-glutamate (PBG) in 1, 2 dichloroethane and dichloroacetic acid on the solvent concentration. Using a photon multiplier and a multi-channel analyser, the probability of detecting a photon at $t = \tau$ within an interval $d\tau$, having first detected a photon at $t = 0$, is measured for various values of τ

and temperature of the solution. From the measurements of the above conditional probability $P_c(\tau)d\tau$, the ratio between the concentrations of the helix and coil forms of PBG can be deduced by numerical analysis up to a constant related to the polarizability of the two different kinds of molecules.

19.0 Atmospheric Affects on Synthetic Aperture Radar Systems

Personnel: J. A. Janzen and H. E. Stanley
Sponsorship: Advanced Research Projects Agency, Research Corporation

The general effects of atmospheric propagation on Synthetic Aperture Radar (SAR) are discussed, with special attention given to the degradation of azimuth resolution by small and moderate scale eddies. Simple closed expressions are found for the half power azimuth resolution and the horizontal beam canting in terms of the level of atmospheric refractive turbulence and basic SAR design parameters. In the development, the horizontal projection of the Obukhov-Kolmogorov spectrum is assumed to be valid to eddy sizes of 5km. The resultant antenna aperture phase covariance function is then approximated by a gaussian. Similarly, the point output response of the SAR is gaussian approximated and an associated angular covariance function is found. The phase error modulated Fourier transform relations of Brown and Palermo are then used to derive the final results. The limitations of the model are discussed and graphic results for a nominally designed system are given. The similarity of SAR to holography has been exploited to clarify the development.

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J. A. Janzen, "Atmospheric Affects on Synthetic Aperture Radar Systems," S. M., Department of Physics, August 1970.

H. I. Botman, "High-Temperature Expansions and Methods of Series Analysis," S. B., Department of Physics, June 1970.

M. L. Jennings, "Experimental Problems in Raman Spectroscopy of Biopolymers," S. B., Department of Physics, June 1970.

S. H. Kinney, Jr., "A Chain of Classical Heisenberg Ferromagnets and an Alternate Version of Monte Carlo Integration," S. B., Department of Physics, June 1970.

R. M. Lucash, "High Temperature Series Expansions in the Spherical Model" S. B., Department of Physics, June 1970.

C. C. Lo, "Intensity Correlation Measurement of Light Scattered From a

Solution of Poly-γ-Benzyl-L-Glutamate in 1,2 Dichloroethane and Dichloroacetic Acid," S. B., Department of Physics, June 1970.

D. L. Njus, "Mechanism of Nerve Excitation," S. B., Department of Physics, June 1970.

Publications:

Books

H. E. Stanley, Introduction to Phase Transitions and Critical Phenomena, Oxford University Press (a book in the "International Series of Monographs on Physics," W. Marshall and D. H. Wilkinson, Eds.).

H. E. Stanley, Readings in Phase Transitions and Critical Phenomena, a companion volume consisting largely of reprinted articles and a 2000-entry bibliography.

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H. E. Stanley, "Expansion Methods in Critical Phenomena." In Phase Transitions and Critical Phenomena, C. Domb and M. S. Green, Eds., (Academic Press, N. Y.)

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D. D. Betts, C. J. Elliott, and M. H. Lee, "Critical Properties of a Quantum Lattice Model," Can. J. Phys., 48, 1566 (1970).

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D. D. Betts, R. V. Ditsian, C. J. Elliott, and M. H. Lee, "Critical Behavior of the XY Model of a Ferromagnet," J. D. Phys. (1970).

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K. Matsuno, "Collective Excitation in the Critical Region of Second Order Transitions", (in press).

IX. ORDER-DISORDER PHENOMENA

Faculty:

* C. W. Garland, Professor, Chemistry

Research Staff:

* Dr. E. Litov, Research Associate, Chemistry
* Dr. L. Mistura, Research Associate, Chemistry
* Dr. R. J. Pollina, Research Associate, Chemistry
  Dr. B. A. Strukov, Visiting Scientist

Graduate Students:

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* C. K. Choo, Research Assistant, Chemistry
  D. Eden, Research Assistant, Chemistry
* B. B. Weiner, Research Assistant, Chemistry

Support Staff:

  Janet Pollock, Secretary, Chemistry

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  Dr. E. Litov, Research Associate, Chemistry (Now at Bar-Ilan University, Ramat-Gan, Israel)

  Dr. B. A. Strukov, Visiting Scientist (Now at Lomonsov State University, Moscow, USSR)

  B. B. Weiner, Research Assistant, Chemistry (Now at State University of New York, Stony Brook, N. Y.)

Degrees Granted:

  B. B. Weiner, Ph.D., Chemistry, September 1970

Sponsorship:

* Advanced Research Projects Agency, SD-90, DSR 75104
  National Science Foundation Grant, GP-7738, DSR 70706 (until 1 January 1970) and GP-13548, DSR 72061 (current)
  Research Laboratory of Electronics, supported by the Joint Services Electronics Program under Contract DA28-043-AMC-02536(E), DSR 70050

Research Report

1.0 Ultrasonics

Personnel: C. W. Garland; E. Litov, L. Mistura, R. J. Pollina, B. A. Strukov; C. K. Choo, D. Eden

Sponsorship: Advanced Research Projects Agency, National Science Foundation

1.1 Liquid-Vapor Critical Point in Xenon

Sound velocity and attenuation measurements have been carried out by D. Eden, using a pulse interferometer in which the received signal is compared with a coherent reference signal. Phase-sensitive detection and signal averaging provide a very high signal-to-noise ratio, which is needed near a critical point. Data have been obtained along several isotherms and isochores at frequencies between 0.4 and 5 MHz, but the analysis has so far been limited to a single near-critical isotherm at temperatures from 0.08 to 20°C above T_c. Velocity dispersion as well as non-classical attenuation was observed in the ultrasonic range, and comparison could also be made directly with recent hypersonic Brillouin measurements by Benedek and Cannell.

Theoretical work by L. Mistura, which closely parallels a recent formulation by Kawasaki, leads to the prediction that the critical attenuation per wavelength should depend on temperature and frequency through a single reduced variable $\omega^* = \omega/\omega_D$. The characteristic frequency ω_D is defined by $\omega_D = (2\Lambda/\rho C_p)\xi^{-2}$, where Λ is the coefficient of thermal conductivity, C_p is the specific heat, and ξ is the long-range correlation length. On the basis of available information, we have determined that $\omega_D = a\,\epsilon^2$, where $\epsilon = (T-T_c)/T_c$ and a is a constant. Using this expression for ω_D, we find very good agreement between the experimental α_λ results and numerical calculations over the range $10^{-4} < \omega^* < 10$. Very close to the critical point ($10 < \omega^* < 10^3$) the current theory breaks down, but our experimental results appear to be consistent with the asymptotic high-frequency limiting behavior estimated by Kawasaki. There is good agreement between ultrasonic and hypersonic data for the sound wave attenuation but some discrepancies in the velocity dispersion (which can be analyzed in terms of the same theoretical model).

1.2 Ferroelectric Transition in KH_2PO_4

Experimental work is now complete: the velocity and attenuation of 15 MHz ultrasonic shear waves have been investigated as a function of the temperature and the electric field applied along the polar axis of KDP single crystals. These data have been analyzed to give the static dielectric susceptibility χ and the polarization relaxation time τ. The χ values are in fairly good agreement both above and below T_c with the predictions of the Silsbee-Uehling-Schmidt (SUS) model. However, the τ values show a temperature dependence which cannot be readily interpreted in terms of the SUS model. Comparison with comparable data for KD_2PO_4 indicate that proton tunneling plays an important role in KH_2PO_4.

1.3 High-Temperature Transition in $BaTiO_3$

Barium titanate is a displacive perovskite-type ferroelectric which undergoes a first-order transition to a cubic paraelectric phase at 129.9°C. Large, oriented single crystals were obtained from Dr. A. Linz of the Materials Center's Crystal Physics Group. These crystals were poled, and all data below T_c were obtained on single domain crystals. The dielectric constant ϵ_c follows a Curie-Weiss plot both above and below T_c ($T_o^- = 139$°C in the ferroelectric phase and $T_o^+ = 116$°C in the paraelectric phase). Ultrasonic measurements were restricted to the velocity u and the attenuation α of longitudinal waves propagating along the a axis since this wave is piezoelectrically coupled to the dielectric susceptibility along the c axis. The elastic stiffness $c_{11} = \rho u^2$ shows a small anomaly in its temperature dependence just below T_c and a finite change in value at T_c as one would expect for a displacive transition. Attenuation data were obtained as a function of temperature in the range 90-310 MHz. Below T_c, these data were well described by $\alpha - \alpha_o = \omega^2(A + B\Delta T^{-1/2})$, where α_o is a temperature and frequency independent background attenuation of 0.25 dB cm^{-1} and $\Delta T = T_o^- - T$. Above T_c, the frequency and temperature dependences of α are weak and do not follow any simple expression. Indeed, the attenuation just above T_c appears to be independent of temperature over a range of a few degrees. Further analysis and interpretation of these data is in progress.

1.4 High-Pressure Attenuation in Solids

Preliminary measurements of the attenuation α near the lambda line in NH_4Cl at high pressures (see the paper by Garland and Snyder) indicated that

there were interesting changes in the peak value of α as one moved up along the transition line. This view is reinforced by the recent volume measurements reported in section 3.0 below. Dr. Pollina joined this group last spring and is in the process of constructing new and more precise temperature and pressure control equipment. In addition, it is planned to use more sophisticated ultrasonic techniques such as those mentioned in section 1.1 above. The immediate goal is to study the attenuation in NH_4Cl as a function of temperature and frequency along the "critical isobar" $p \simeq 1500$ bar.

2.0 Dynamical Calorimetry

Personnel: C. W. Garland; A. Bonilla
Sponsorship: Advanced Research Projects Agency, National Science Foundation

Development of a phase-sensitive detection technique for measuring specific heats near a critical point is in progress. It is planned to study chromium near its antiferromagnetic transition at 1 atm and also at high pressures. The method involves heating a wire sample with a low-frequency, low-voltage ac current. The temperature variation of the sample, which is inversely proportional to the heat capacity, can be measured with considerable precision with a thermocouple and lock-in detector. The resistance of the wire, which is also a sensitive indication of the ordering process, can be measured simultaneously. Difficulties with interfering induction effects were encountered and finally solved during an extensive series of test measurements. Checks on the effect of pressure on the sensitivity of the thermocouple are now in progress, and measurements on Cr will begin soon.

3.0 Pressure-Volume Measurements

Personnel: C. W. Garland; B. B. Weiner
Sponsorship: Advanced Research Projects Agency, National Science Foundation

Variations in the length L of an NH_4Cl single crystal in the vicinity of the order-disorder transition have been determined. A three-terminal capacitance technique has been developed for high-pressure work, and the method is capable of resolving changes in L on the order of 1 ppm. Two

single crystals were studied; altogether, eleven isotherms from 250 to 273°K and two isobars at 1636 and 2841 bar were investigated.

A small first-order transition with no hysteresis was observed at 250.04°K and 833 bar where $\Delta L/L \approx 3.8 \times 10^{-4}$. The first-order discontinuity is superimposed on an overall lambda-like variation in L. At 254.11°K and 1303 bar the first-order change $\Delta L/L$ amounts to only 1.7×10^{-4}. At a "critical point" near 255.75°K and 1493 bar, L varies continuously, but κ_T and α appear to diverge. At higher pressures, the variation in L at the transition becomes progressively more gradual, and finite maxima in κ_T and α were obtained at the transition. These maxima decrease in magnitude as one proceeds further along the transition line. An average value of 1.96×10^{-6} bar^{-1} was found for the linear isothermal compressibility in the disordered phase. For the two high pressure isobars, a value of $\approx 8 \times 10^{-5}$ deg^{-1} was found for the linear isobaric thermal expansion coefficient in the disordered phase. Smooth-curve values for the variation in L were established over a wide range of p and T in both the ordered and disordered phase.

The experimental work on this problem is now complete, and a brief account of the principal new results has recently been submitted as a Physical Review Letter. Analysis of the data in terms of two new (as yet unpublished) theoretical studies is in progress and a complete account of the work will be submitted for publication in the near future.

4.0 Libration in Ammonium Halide Crystals

Personnel: C. W. Garland; B. B. Weiner

Sponsorship: Advanced Research Projects Agency, National Science Foundation

An infrared investigation of the ammonium halides by Schumaker and Garland has indicated that the librational potential function is more anharmonic than Nagamiya's model would predict. A careful analysis of this model, which is based on electrostatic interactions plus nearest-neighbor overlap repulsion, shows that it is not possible to reproduce the observed overtone frequencies with a potential based on a linear combination of the two lowest spherical harmonics of proper symmetry (Y_4 and Y_6). It appears that hydrogen bonding plays an important role, and we have developed a semi-empirical potential function which is able to predict the spectroscopic observations very well. The assumed potential for small-angle rotations of the tetrahedral ammonium ion about its equilibrium position in a CsCl-type cubic lattice is

$$V = A(r)\,[(\xi^2 + \eta^2 + \zeta^2) - B(\xi^2\eta^2 + \xi^2\zeta^2 + \eta^2\zeta^2)]$$

$$+ (2p-1)\,C(r)[(\xi^2 + \eta^2 + \zeta^2) - 2(\xi^2\eta^2 + \xi^2\zeta^2 + \eta^2\zeta^2)]$$

where the second term represents the weak ($C/A \sim 0.06$), order-dependent, nearest-neighbor NH_4^+-NH_4^+ interaction and the first term is an empirical representation of all the other interactions (largely NH_4^+-X^- contributions). The crucial difference between this expression and Nagamiya's potential is the absence of pure quartic terms and the relative importance of the coupling terms ($B = 5.09$). Further details are given in a paper in the Journal of Chemical Physics.

Thesis:

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Publications:

A. Bonilla, C. W. Garland, and N. E. Schumaker, "Low-Temperature X-Ray Investigation of NH_4Br", Acta Cryst. A26, 156 (1970).

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C. W. Garland, "Ultrasonic Investigation of Phase Transitions and Critical Points", Physical Acoustics, W. P. Mason and R. N. Thurston, eds. (Academic Press, New York, 1970), Vol. 7, Chap. 2.

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C. W. Garland, D. Eden, and L. Mistura, "Critical Sound Absorption in Xenon", Phys. Rev. Letters, in press.

X. MOLECULAR CRYSTALS

Faculty:

R. J. Silbey, Associate Professor, Chemistry

Research Associates:

B. Sharf (Sept. 1, 1969 -)

Graduate Students:

M. Grover, NSF Predoctoral Fellow, Chem.

P. Chalmer, NSF Trainee, Chem.

* J. Schroeder, Research Assistant, Chem.

* C. Sloane, Research Assistant, Chem.

S. Rackovsky, NSF Predoctoral Fellow, Chem.

J. Herzfeld, Research Assistant, Chem.

Sponsorship:

* Advanced Research Projects Agency, SD-90, DSR 75108 (from February 1, 1968)

National Science Foundation, GP-8387, DSR 70993 (from June 1, 1968)

Petroleum Research Fund of American Chemical Society, #3574-AC-5, DSR 71152 (from Sept. 1, 1969)

Research Report:

During the past year, we have calculated the exciton band structure of the lowest exciton states of crystalline naphthalene and anthracene using the Ewald method to evaluate the dipolar interaction sums. We have taken into account configuration mixing and the boson nature of the excitons. These calculations will be used to evaluate the exciton density of states for comparison with optical absorption experiments.

We have been interested in the interaction of vibrational and electronic modes in molecules and molecular crystals. We have continued our work on the Jahn Teller effect (the vibronic interaction between degenerate electronic states in non-linear molecules) and have considered the effect of quadratic terms in the vibronic coupling. We have also been using Green's function methods (as well as other many-body techniques) to calculate the

energy shifts and absorption spectra of molecules which exhibit the Jahn-Teller (or pseudo Jahn Teller effect).

In addition, we have just completed a calculation of the rate of energy transfer via excitons in molecular crystals. Using a linear exciton-phonon coupling, we have derived an approximate equation of motion for the probability of energy transfer from one site in a crystal to any other site. Using this equation, we predict a change from coherent transport at low temperatures to incoherent ("hopping") transport at high temperatures. The qualitative behavior of the diffusion coefficient is in accord with the available experimental evidence.

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I. SOLID STATE STUDIES GROUP

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* Mildred S. Dresselhaus, Professor, Electrical Engineering
* C. G. Whitney, Assistant Professor, Electrical Engineering

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S. Iwasa, Research Associate, Physics
N. J. Parada, Research Affiliate, Electrical Engineering

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D. Cammack, Graduate Student, Electrical Engineering
* D. S. Choo, Research Assistant, Electrical Engineering
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B. L. Heflinger, Graduate Student, Electrical Engineering
L. Johnson, Graduate Student, Electrical Engineering
T. Kaplan, Graduate Student, Electrical Engineering
* E. K. Li, Graduate Student, Electrical Engineering
* P. G. McMullin, Graduate Student, Electrical Engineering
* F. P. Missell, Research Assistant, Physics
G. R. Ohlhoeft, Undergraduate Student, Electrical Engineering
D. A. Platts, Research Assistant, Electrical Engineering
* C. L. Rieck, Research Assistant, Physics
L. E. Schmutz, Undergraduate Student, Electrical Engineering
D. Schroeder, Graduate Student, Electrical Engineering
A. Tachagumpuch, Graduate Student, Physics
W. W. Toy, Undergraduate Student, Physics
J. C. Tsang, Teaching Assistant, Electrical Engineering

Support Staff:

Collen Keough, Secretary, Electrical Engineering
Thalia P.Stone, Secretary, Electrical Engineering

Personnel who have left:

S. Iwasa, Research Associate, Physics (Now at Energy Conversion Devices,

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D. Schroeder, Graduate Student, Electrical Engineering (Now at Pensacola Air Force Base, Pensacola, Florida)

Degrees Granted:
D. Cammack, S.M., Electrical Engineering, June 1970
D. Schroeder, S.M., Electrical Engineering, June 1970
C. G. Whitney, Ph.D., Physics, June 1970

Sponsorship:
Office of Naval Research, Nonr-1841(72): NR018-106 DSR 72141
Army Research Office-Durham, DA31-124-ARO(D)92, DSR 79489
* Advanced Research Projects Agency, SD-90, DSR 72214, DSR 72217
California Institute of Technology, Jet Propulsion Laboratory, NASA 7-100/RD-26, DSR 72535
U. S. Air Force, Lincoln Laboratories Account 11195

Research Report

1.0 Electronic and Optical Properties of Materials

Personnel: G. W. Pratt, Jr, C. G. Whitney, P. G. McMullin, E.K. Li, D. S. Choo and D. Cammack

Sponsorship: Army Research Office-Durham, Advanced Research Projects Agency

Laser emission from optically pumped p-type PbSe at 4.2°K has been studied as a function of (110) uniaxial stress. This splits the (111) multi-valley degeneracies of the valence and conduction bands. Intervalley transfer of holes or electrons requires the emission of a momentum conserving phonon. Energy conservation forbids this until the valley splitting equals the energy of the intervalley phonon. Two separate lines are observed at low stress corresponding to emission from the energy gaps at the (111) and ($1\bar{1}\bar{1}$) zone edges. The energy difference between these lines is tunable and linear in the strain. When this difference equals the (200) intervalley phonon energy, optical transitions originating in the higher conduction band valley cease and the intensity of the line originating in the lower conduction band valley doubles. The frequency dependence on strain in this region should give a very accurate measure of the intervalley phonon coupling. In addition the conditions for stimulated emission of intervalley phonons

appear to be satisfied.

A cw GaAs diode laser has been frequency modulated at 150 MHz using compressional ultrasonic waves. These waves were generated in a quartz transducer and transmitted to the active region of the laser where they modulated the refractive index. The FM spectrum was observed using a Fabry-Pecot interferometer (FPI) and showed that very little distortion was present. A modulation index of 7.5 was obtained. Modulation via injection was performed at frequencies up to 1 GHz. The observed spectrum contained both FM and AM and aged well with that calculated for a laser in which both the real and imaginary parts of the dielectric constant are modulated. The rates of AM index to FM index was 0.1. High resolution measurements of the spectral shift of a GaAs laser under pulsed emission were made using an FPI. The experiment was performed at both 4.2°K and 77°K giving more accurate results than are possible with standard techniques. Extension of this technique to room temperature permits the possibility of a pulsed room temperature FM optical transmitter.

The photconductivity of optically pumped PbSnTe is being studied in the narrow energy gap region where electron-hole recombination takes place via LO phonon emission rather than photon emission. It should be possible in this way to obtain a phonon laser. The value of the energy gap is controlled by varying the temperature. A marked change in the mobility is observed near the point where the energy gap goes to zero. It is believed that this is due to the emission of LO phonons by electrons which have been pumped up into the conduction band.

The elastic constants of $Pb_{0.5}Sn_{0.5}Te$ have been studied in the temperature range where the energy gap has been thought to go through zero. An anomaly has been found in the elastic constant C_{44} and no irregularity in C_{11} or C_{12}. The size and nature of the anomaly is theoretically predicted to be determined by the difference in deformation potentials of the bands that are asserted to cross each other. The experimental results confirm the band crossing model and excellent quantitative agrument is obtained.

A high power CO_2 laser has been designed and constructed. Due to the high reflectivity of most metals, almost no energy is absorbed from the beam by the metal itself. Large amounts of energy can, however, be transferred to organic matter on the surface of the metal. Clinical tests have demostrated that dried spores of a very heat resistant variety, when spread on an Al surface and exposed to the CO_2 beam, are very rapidly killed. Other organisms are now being studied. Intense laser radiation appears as an ideal means of producing nearly instantaneous sterilization of metallic objects such as packaging foils, surgical instruments, and metallic containers. No

deterioration of the irradiated objects is observed. Experiments are being extended to observe the effects of Q-switched pulses on biological systems.

A model for vacancy states in PbTe was developed which explained the low temperature transport properties. PbTe experimentally behaves like a dilute metal at low temperatures. The results of this investigation showed that there were no localized states in the energy gap due to either Pb or Te vacancies which are the principal sources of holes and electrons. The study is now being extended to localized states due to impurity atoms at interatitial locations. Knowledge of the properties of vacancy and interstitial states should lead to an understanding of the transport properties of the Pb salts and of such problems as junction degradation.

2.0 Electronic Properties of Amorphous Materials

Personnel: G. W. Pratt, Jr and T. Kaplan

Sponsorship: Office of Naval Research

Conduction in an amorphous Te-Ge system is being studied. The model deals with the establishment of a filamentary current path. Once established, heating of the filament is considered and the diffusion of Ge out of the filament leaving a high conductivity crystallized Te filament behind. The solution of the diffusion equation for Ge is required in a situation where the temperature is a function of time. The time independent heat flow equation in two dimensions with a non linear source term is now being studied.

3.0 Electromagnetic Response of Dielectric and Magnetic Media to Pulsed Electric and Magnetic Fields

Personnel: G. W. Pratt, Jr. and G. Ohlhoeft

Sponsorship: Office of Naval Research

This work is primarily concerned with the electromagnetic response of the earth to pulsed electric and magnetic fields. Measurement of the complex electric and magnetic susceptibilities as a function of frequency allows one to indentify the material responding. In the case of magnetic media a pulsed magnetic field moves domain walls. These walls are usually pinned by imperfections. When the pulse ceases, the magnetization relaxes to its state before the pulse with a characteristic time. It has been possible

to explain several anomalous effects in airborne electromagnetic delection survey by this mechanism.

4.0 Optical Properties of Electronic Materials

4.1 The Fermi Surface and Optical Properties of Arsenic

Personnel: R. W. Brodersen and M. S. Dresselhaus

Sponsorship: Advanced Research Projects Agency, NSF Fellowship, Lincoln Laboratory

The infrared properties of arsenic are of particular interest because of the simultaneous occurrence of a large interband momentum matrix element and a high joint density of states of interband transitions when light is incident along the trigonal direction. A calculation of the infrared reflectivity has shown the measurements of the Fermi surface, magneto-reflection and optical properties to provide a consistent picture for the energy band structure of arsenic. On the other hand, serious discrepancies are found between the magnetoreflection observations and the Lin-Falicov band model, which provides a good representation for the Fermi surface data. Considerable progress has been made in modifying this band model to yield energy bands which are consistent with both the Fermi surface and magneto-reflection measurements.

4.2 The Optical deHaas-Shubnikov Effect in Antimony

Personnel: F. P. Missell, S. Iwasa, A. Javan, L. E. Schmutz and M. S. Dresselhaus

Sponsorship: Advanced Research Projects Agency, NASA Washington Contract 76148

Oscillations in various magnetic and transport properties are observed when a magnetic energy level is made to pass through the Fermi energy. In this connection, a detailed study is being made of the physical properties and mechanisms involved in the manifestation of this effect in the optical reflectivity of solids. Observations have been made of the dependence of the optical deHaas-Shubnikov effect in antimony on temperature, photon energy, crystal orientation and on sample geometry. By using low temperatures and a

high resolution magnetoreflection technique, it has been possible to study the asymmetric lineshapes associated with the optical deHaas-Shubnikov resonances. Whereas the observations above $\sim$ 10°K can be understood in terms of a model based on oscillations in the carrier density, it is necessary to invoke oscillations in the relaxation processes to explain the data obtained at low temperatures on the highest quality samples.

4.3 Differential Reflectivity Studies in Tellurium

Personnel: D. A. Platts and M. S. Dresselhaus

Sponsorship: Advanced Research Projects Agency

Despite the great recent interest in the energy band structure of tellurium, almost no experimental information is available except for the two highest valence bands and the lowest conduction band about the H point. An attempt is being made to obtain new and different information about the tellurium energy bands through detailed differential reflectivity measurements at infrared and visible frequencies.

4.4 Optical Properties of Anisotropic Solids

Personnel: C. L. Rieck, W. J. Scouler, and M. S. Dresselhaus

Sponsorship: Advanced Research Projects Agency, Lincoln Laboratory

Experimental techniques have been developed to measure the optical reflectivity of anisotropic solids in the photon energy range $2 < h\nu < 10eV$ using polarized light. Preliminary results have been obtained on the semimetal antimony. Measurements on several anisotropic semiconductors and group V semimetals are planned.

4.5 Frequency Dependence of Conductivity in Graphite

Personnel: A Tachagumpuch and M. S. Dresselhaus

Sponsorship: Advanced Research Projects Agency

Although the large anisortopy (factor of 10^4) in the conductivity of pyrolytic graphite is of interest for device applications, the basic

mechanism associated with this property is not understood. By studying the frequency dependence of the conductivity for various temperatures, we hope to be able to determine whether band conduction or a hopping mechanism is responsible for the low c-axis conduction. Preliminary results have so far been obtained at room temperature for frequencies up to 10^{10} Hz.

4.6 Application of AC Temperature Technique to Magnetic and Calorimetric Measurements in Magnetic Materials

Personnel: J. C. Tsang, R. R. Oder, and M. S. Dresselhaus

Sponsorship: Advanced Research Projects Agency, Air Force Office of Scientific Research and Development, NSF Fellowship

The instrumentation has been completed for making sensitive measurements of the magnetization in the temperature range $1.2<T<10°K$ using the AC temperature technique; the instrumentation for the complementary calorimetric measurements is almost in working order. To calibrate and gain experience with the equipment, preliminary measurements are being carried out on the ferromagnetic metal Ni and on the insulating ferromagnet YIG.

4.7 High Resolution Study of the Magnetoreflection Spectrum in Graphite

Personnel: B. L. Heflinger, F. P. Missell, S. Iwasa, W. W. Toy, and M. S. Dresselhaus

Sponsorship: Advanced Research Projects Agency, NASA Washington Contract 76148, NSF Fellowship

On the basis of earlier high resolution magnetoreflection studies in graphite, it was concluded that the band parameter γ_3, which controls the warping of the Fermi surface, is so large as to preclude the possibility of using any form of perturbation theory in dealing with the magnetic energy levels in graphite. Because of the far-reaching consequences of this result, these magnetoreflection measurements have been extended to higher magnetic fields, and, in particular, into the field range $100<H<145$ kG. In so doing, several new inter-Landau level transistions have been observed for both senses of circular polarization of the incident radiation. These new transitions are being used to test the validity of the existing band model. As a result of this investigation, considerable progress has been made in

increasing the sensitivity of the technique by introducing improved laser stability and field modulation detection.

4.8 Electron and Phonon Dispersion Relations in Tellurium

Personnel: G. Dresselhaus and M. S. Dresselhaus

Sponsorship: Advanced Research Projects Agency, Lincoln Laboratory

The Fourier expansion technique has been applied to yield the form of the dispersion relations required by crystal symmetry for the phonon modes and for the electronic energy bands in tellurium. For the phonon spectrum, ample experimental information was available for the evaluation of the Fourier expansion coefficients from Raman scattering data for optical modes at the Γ point, from elastic constant data for the acoustic modes near Γ, and from inelastic neutron scattering data pertaining to a number of high symmetry axes in the Brillouin zone. The quantity of experimental data available for the electronic problem is at present inadequate for making a similar detailed determination of the electronic energy band structure.

5.0 Silicon Solar Cells

Personnel: R. W. Brodersen, D. A. Platts, C. L. Rieck, J. C. Tsang and M. S. Dresselhaus

Sponsorship: California Institute of Technology, Jet Propulsion Laboratory
NASA 7-100/RD-26

A study aimed at improving the performance and increasing the radiation hardness of silicon solar cells for space applications is in progress. In this connection, it has been found that the diffusion of lithium into the solar cells can reduce radiation damage. Extensive studies have been made of both (1) the physical nature of defects, traps and impurities in lithium-doped silicon and (2) the electrical properties of lithium-diffused solar cells. We are now developing a kinetic model which, on one hand, relates the physical properties of the bulk material to the cell performance, and, on the other hand, enables adjustment of cell parameters to optimize the cell performance for specific space applications.

Theses:

C. G. Whitney, "The Behavior of Laser Modes in a Medium with Time Varying Dielectric Constant", Ph.D. Department of Physics, June 1970.

D. Schroeder, "Emission Spectroscopy Utilizing a High Power CO_2 Laser System", S.M., Department of Electrical Engineering, June 1970.

D. Cammack, "Theory of Laser Action in a Stressed Semiconductor", S.M. Department of Electrical Engineering, June 1970.

Publications:

G. W. Pratt, Jr. and A. Das, "Anomalous Behavior of the Elastic Constants of $Pb_{0.5}Sn_{0.5}Te$ in the Zero Gap Region", Journal of Phys. and Chem. of Solids, in press.

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M. S. Dresselhaus, "Electronic Properties of the Group V Semimetals", Proceedings of the Conference on the Physics of Semimetals and Narrow Gap Semiconductors, Dallas, Texas, 1970, in press.

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M. Maltz and M. S. Dresselhaus, "Magnetoreflection Studies in Bismuth", Phys. Rev., in press.

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II. SEMICONDUCTOR MATERIALS AND DEVICES

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  A. C. Smith, Professor, Electrical Engineering
  R. D. Thornton, Professor, Electrical Engineering
* F. O. Arntz, Associate Professor, Electrical Engineering
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  C. J. Dillon, Graduate Student, Electrical Engineering
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  R. L. Guldi, NSF Trainee, Electrical Engineering
  A. R. Hartman, Research Asst., Electrical Engineering
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C. J. Yankowski, Student Technician, Electrical Engineering
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Jarmilia Z. Hrbek, Secretary (part-time), Electrical Engineering
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Personnel who have left:

Professor B. D. Wedlock (on leave)
Professor D. L. Smythe (to Nova Devices, Inc.)
Professor J. S. Moore (to Micro-Bit Corp.)
W. J. Gajda, Jr. (returned to Notre Dame faculty)
L. A. Goodman (to RCA Laboratories, Princeton, N.J.)
T. L. Credelle (to RCA)
R. J. Lafond (to armed services)
R. C. Busby (to National Semiconductor Corp.)
C. J. Dillon (returned to industry)
T. F. Hafer (to Iowa State Univ.)
E. Lombrozo (to industry in Mexico)
B. P. Mathur (to graduate study in Amorphous Semiconductor group Electrical Engineering Dept.)
R. C. Walleigh (graduated)
C. J. Yankowski (graduated)

Degrees Granted:

C. G. Fonstad, Jr., PhD., Electrical Engineering, Sept. 1970
W. J. Gajda, Jr., Ph. D., Electrical Engineering, Sept. 1970

L. A. Goodman, Ph.D., Electrical Engineering, Feb. 1970
R. White, Ph.D., Electrical Engineering, Feb. 1969
T. L. Credelle, SM, Electrical Engineering, Sept. 1970
R. J. Lafond, SM, Electrical Engineering, June 1970
B. P. Mathur, SM and EE, Electrical Engineering, Feb. 1970
E. Prahl, SM and EE, Electrical Engineering, Feb. 1970
T. F. Hafer, S.B., Electrical Engineering, June 1970
P. Hermansen, S.B., Electrical Engineering, June 1970
E. Lombroza, S.B., Electrical Engineering, June 1970
J. Shuster, S.B., Electrical Engineering, June 1970

Sponsorship:

* Advanced Research Projects Agency, SD-90, DSR 75112, 75115;
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Office of Naval Research, N00014-67-A-0204-0010, DSR 70421;
N00014-67-A-0204-0029, DSR 71988
Air Force Office of Scientific Research, AFOSR-68-1571, DSR 71013
U. S. Department of Transportation, C-85-65, DSR 76104
National Air Pollution Control Administration, EHS-70-112, DSR 72524
MIT Sloan Fund for Basic Research
NSF Traineeships

Research Report

Survey

The general theme of the work undertaken here is the relationship between electronic device capabilities and limitations, and the materials employed. These capabilities and limitations may be inherent in the material itself, or may stem from problems of associated technology. Our efforts therefore span the range from investigations of ultimate circuit performance of an existing or newly conceived device, in terms that relate closely to its structure, all the way to attacking technological problems of importance in determining ultimate device performance.

1.0 Optically Pumped Absorption in Cadmium Sulfide

Personnel: Professors F. O. Arntz, R. B. Adler; L. A. Goodman

Sponsorship: Advanced Research Projects Agency

A number of materials are known to exhibit changes in absorption upon exposure to light. This effect, often called photochromism, does occur in the well-known semiconductors; but in these the absorption changes are too feeble to investigate with conventional optics and electronics. However, there has been reason to develop techniques for such measurements since these slight changes in absorption provide a particularly direct means of investigating defect centers in semiconductors.

This study has concentrated on the development of equipment and techniques for such investigations and has applied these to the study of defects in single-crystal cadmium sulfide.

As in other crystalline semiconductors, in cadmium sulfide adsorption of light having energy less than the fundamental gap arises from interaction of light with the lattice and with defects. Since the occupancy of defect-related electron states is affected by exposure to light of certain wavelength ranges, such exposures have an effect on the absorption of light subsequently incident on the material.

The measurements are performed in a differential manner. The sample is alternately prepared for absorption measurements by exposure to band-gap radiation and infra-red radiation. In detail, a sample is cycled through an exposure sequence of four components:

i) typically one second exposure to an intense band of radiation (pumping radiation) in the vicinity of 2.4 eV, the gap of CdS.

ii) A precisely timed one second exposure to sampling radiation of low intensity monochromatic light

iii) A one second exposure to intense "bleaching" radiation, in the infra-red, and

iv) another precisely timed exposure to the sampling radiation.

The sampling radiation, provided by a spectrometer, is chopped at 400 hz. The detected signal is processed by a differential amplifier and a lock-in-amplifier. Digital techniques are employed to integrate the lock-in amplifier output during each of the sampling intervals and to obtain the difference between these integrated values for each exposure cycle. The digital techniques permit accumulation of data over many exposure cycles, thereby allowing investigation of very slight photochromic effects. Time dependent variations in the monochromatic beam intensity, normally a serious problem at low measuring frequencies, are discriminated against by using a spectrometer modified to provide split double-beam optics, and by employing matched PbSe detectors in a bridge network for input to the signal processor.

High purity and ultra-high purity single crystals of CdS from Eagle-Picher Industries (Miami, Oklahoma) and Professor F. Chernow at the University of Colorado were studied over a wide range of temperatures by the pumped absorption (photochromic) technique described above. At least two different class II recombination centers--i.e. those having a small capture cross section for the majority carrier and large one for the minority carrier--were detected by this technique. One of these, the well-known "sensitizing center" accounts for two spectral bands in the pumped absorption spectra. It is particularly striking to compare the latter results with results obtained by employing the technique of optical quenching of photoconductivity in the study of the same crystals. In the vicinity of room temperature the results are quite similar but at low temperatures ($90^{o}K$) the low energy peak (0.87 eV) disappears from the photoquenching data. This comparison confirms the model employed to explain the nature of the "sensitizing center". At low temperatures, according to this model, radiation of 0.87 eV lifts a deep hole from its ground state to a shallow level proximate to the valence band. However at room temperature, phonons are available to subsequently transfer this hole to the valence band and thereby contribute to photoquenching (i.e. elimination of conduction electrons by recombination). Of course in the pumped absorption experiment, transfer of the hole subsequent to excitation to the shallow level is of no consequence. Therefore,

the pumped absorption structure remains essentially unchanged.

A second recombination center, first reported in L. Goodman's doctoral thesis, is manifested in pumped absorption measurements at an energy of 0.7 - 0.8 eV. Comparison with photoquenching data allows identification of the process as an ionizing transition involving transfer of a hole from the ground state of the defect into the valence band. This center is tentatively identified as a doubly ionizable Cd vacancy with a closely associated singly ionizable group III or group V donor. As such it is similar to the "A center" found in ZnS.

Slight photochemical effects were observed in one ultra-high purity crystal of CdS. Frequent exposure to band gap radiation over a two week interval resulted in a small (roughly 5%) change in the pumped absorption spectrum (for further details see Thesis, L. A. Goodman).

2.0 Interaction of Successive Diffusions

2.1 Phosphorus and Boron in Si

Personnel: Professor R. B. Adler; B. P. Mathur, E. Prahl, J. Schuster

Sponsorship: Advanced Research Projects Agency

The effect of a second diffusion in "enhancing" or "retarding" the diffusion of the first one in a variety of sequential multiple-diffusion process for integrated-circuit planar transistor fabrication has been under study for some years, here and elsewhere. For the most common elements Boron and Phosphorous in Silicon, the effects are especially complicated.

A model for the "retardation" effect, observed for diffusion at temperatures near 1100°C in p^+n^+p structures with heavily doped bases, has been proposed. It is based upon the nucleation of phosphorus precipitates by non-conservative growth of dislocations generated throughout the emitter region. This model is based on that proposed by J. E. Lawrence originally, but expands considerably upon it by: (1) allocating all of the precipitation of base phosphorus to virtually the entire region occupied also by the boron emitter; and (2) allowing the phenomenon to develop throughout the entire emitter diffusion time (not just during cooling).

The fact that retardation does <u>not</u> occur in n^+p^+n structures of otherwise similar fabrication cannot yet be given a "fundamental" explanation, but rests upon the experimental fact that Boron (unlike phosphorus)

does not ever appear to precipitate in the silicon lattice at other than locations extremely close to the surface at which it is introduced. For further details and some theoretical support see: Thesis (E. Prahl).

A model for the "enhancement" effect observed at diffusion temperatures near 1100°C in n^+pn, p^+np, n^+np and p^+pn structures is based upon a similar picture. In this case, however, the non-conservative growth of dislocations, originating from the "emitter" region and growing through the "base" produces vacancies whose presence (not flux) increases the diffusion coefficient of the "base" impurity. Again the process takes place during the entire "emitter" diffusion cycle, and not just during the cooling time. An approximate theory for this model has been worked out by Hu and Yeh of IBM.

Because the elastic limit increases at lower temperatures, it might be thought that at lower diffusion temperatures (800°-900°C) the dislocations responsible for both the "enhancement" and "retardation" effects would not form. The cooperative diffusion effects would then vanish. Experiments by Ehlenberger at Motorola on very shallow npn and pnp structures at these low temperatures have shown respectively large "enhancement" effects (npn) and negligible interaction (pnp). Independently we have observed the same large npn "enhancement" at 900°C in structures as deep as those normally encountered at 1100°C. An examination of the Hu-Yeh theory for its temperature dependence is in progress to determine whether the general model which seems valid at about 1100°C remains so at 800°C-900°C.

2.2 Arsenic and Gallium in Ge

Personnel: Professor R. B. Adler; E. Vincent

Sponsorship: Advanced Research Projects Agency

Work on the diffusion of Ga into Ge has become necessary, and the appropriate system is still being set up.

3.0 Physical Effects of X-ray Topographic Evaluation of Interface Strain from Passivating Layers on Silicon

Personnel: Professor R. B. Adler; J. H. Serebrinsky (absent); W. J. Gajda, Jr.

Sponsorship: Advanced Research Products Agency

The mathematical analysis of thermal stress concentration at the edges of a "masking window" in an insulating layer on silicon has been completed, and accepted for publication (see Publications, J. H. Serebrinsky, and Thesis, W. J. Gajda, Jr.). The linear elastic model predicts maximum stresses at the interface edge of 10^9 dy/cm^2, with shear components important. Experiments with monochromatic infra-red transmission show a marked anomaly in the region near the edges where the stress is presumably large, and first-order theory suggests that piezo-absorption does take place.

Notwithstanding the limitations of the linear, continuous elastic model employed, the above results, on balance, point to the serious possibility that some reported phenomena in semiconductor devices can be understood as edge-stress dependent processes.

The theory of X-ray scattering and topographic contrast in thin ($\mu t<1$) samples of strained silicon has been carried out using a "deformed Darwin" model of the strained crystal (see: Thesis, W. J. Gajda, Jr.). The essential features of the work include:

1) A reinterpretation of X-ray topographic contrast which focusses attention upon the angular reflection spectrum of the crystal in relation to the angular divergence of the incident beam. With a given moderate angular divergence of the incident beam, increasing the crystal "disorder" produces first a decrease in the integrated scattered intensity, and then an increase. The initial decrease is attributed to loss of coherency in the scattered waves arising from portions of the incident beam at small angular deviations from the Bragg condition; the subsequent increase arises from increased disordered scattering of portions of the incident beam at larger angular deviations from the Bragg condition.

2) An application of this point of view, involving "decreased coherency" competing with "increased angular response", to strained crystals, by noting that "disorder" is large wherever the gradient of the strain in a direction normal to the scattering planes is large. Here the scattered intensity will be "large", from the increased angular response. At nearby places, where the appropriate strain gradient is small, decreased coherency causes a drop in scattered intensity. The dark-light banding phenomena found in images of thin samples locally strained by oxide steps is thus accounted for.

3) Showing both experimentally and theoretically that, besides edge-contrast effects, area- and mixed-contrast effects are not negligible.

4) The first systematic categorization of basic contrast parameters in SiO_2-Si topographs, as functions of oxide growth temperature and thickness.

5) Some discussion of topographic results on ion-implanted silicon.

4.0 Electron-Beam Irradiated Si Diodes (EBIRD's)

Personnel: Professor R. B. Adler; P. Hermansen

Sponsorship: Advanced Research Projects Agency

An analytical study is being made of the possibility of using a Si planar EBIRD as a CW power amplifier at radio frequencies. Linear operation is not required, but high power output at moderate dissipation is essential. Both thermal design and diode efficiency in "Class C" service with a tuned load are being considered. Only tentative results are available thus far.

5.0 Nuclear Magnetic Resonance in Solids

5.1 Knight Shift in Lead Telluride

Personnel: C. R. Hewes, S. D. Senturia, A. C. Smith, R. B. Adler
Sponsorship: Office of Naval Research

A report of the preliminary phase of this work, including measurements of the principal features of the Pb^{207} and Te^{125} Knight shifts in n- and p-type PbTe together with the basic theory required to understand the observed shifts, has now been published.

The second phase of this work, a detailed quantitative study of the Pb^{207} Knight shifts, is nearly complete. A set of 22 high-quality samples have been prepared covering carrier concentrations between 10^{17} and 10^{19} p-type and 10^{17} and 1.5×10^{18} n-type. In the course of preparing and evaluating these samples, it was discovered that p-type material can be completely compensated by powdering, while n-type material is not affected by similar handling. This leads to the postulation of deep, damage-induced donor levels in the PbTe energy gap.

The Pb^{207} nuclear resonance has been measured in each sample between 4.2°K and room temperature. The data have been analyzed in terms of an extremely detailed energy band model of the valence and conduction bands of PbTe. We developed this model from k·p theory in terms of eight parameters which were chosen to fit the observed low temperature values of the Knight shift, the band-edge masses and g-factors, and the Shubnikov - de Haas periods and effective masses. This model can be extrapolated to higher temperatures, permitting separation of the Knight shift due to carriers in the L-point valence band from the contribution of carriers in a second valence band which becomes occupied above 200°K. Final analysis along these lines is in progress.

5.2 Knight Shift in (PbSn)Te Alloys

Personnel: M. S. Adler, S. D. Senturia, A. C. Smith, R. B. Adler, C. J. Yankowski

Sponsorship: Office of Naval Research

Knight shfits of Pb^{207}, Te^{125}, and Sn^{119} have been observed in a wide variety of p-type samples throughout the range of lead-tin fractions. In working with the alloys it has not been possible to obtain the high degree of quantitative precision characteristic of the data in pure PbTe. Nevertheless, a consistent picture of the variation of the Knight shifts with composition and carrier concentration has emerged. The data support qualitatively the band-crossing model of Dimmock, Melngailis, and Strauss. The principal effect of the alloying on the Knight shift is a reduction as the tin fraction is increased due to the admixture of the L_6^- state into the L_6^+ state. Analysis of the data is now under way in order to determine whether it is possible to extract new information on the alloy energy band parameters near the band-crossing region.

Mr. Yankowski has examined the effects of doping $Pb_{.5}Sn_{.5}Te$ with copper. His experiments indicate that copper can compensate up to 10^{18} holes. Excess copper above this amount precipitates into non-active sites over a period of a few days.

5.3 NMR in Ferroelectric $Na_xK_{1-x}TaO_3$

Personnel: R. Siegel, S. D. Senturia, A. C. Smith, R. B. Adler, E. Prahl

Sponsorship: Office of Naval Research

Initial attempts at observing quadrupole splittings of Ta^{181} in the ferroelectric state of sodium-potassium tantalate samples have not been successful. Two alternate paths have been investigated, with interesting results.

Quadrupole splitting of Li^7 in $KLiTaO_3$ mixed crystal have been observed at helium temperature. Satellites from two orthogonal ferroelectric domains are visible. Similar splittings in a new, better quality sample are being studied as a function of temperature in order to determine the temperature dependence of the spontaneous polarization.

A second approach to the study of the phase transitions in the ferroelectric tantalates has been to examine the spin-lattice relaxation times of the various nuclear species. Mr. Prahl and Mr. Siegel have assembled apparatus for implementation of the tone-burst method of measuring relaxation times. This method involves a field-modulation sequence which enables the transient behavior of a spin system to be studied with our regular absorption spectrometer.

Relaxation time measurements were first carried out on Nb^{93} in a

K $Nb_xTa_{1-x}O_3$ sample. The relaxation time shows a marked decrease from the non-polar to the polar state, as observed in other materials by Rigamonti and others. The interpretation of these observations is in progress.

5.4 NMR Instrumentation

Personnel: S. D. Senturia, M. S. Adler, C. R. Hewes, J. A Murphy

Sponsorship: Office of Naval Research

A complete analysis of the signal and noise characteristics of a marginal oscillator spectrometer has been carried out and prepared for publication. The principal result of this work has been the clear identification of the mixing of 1/f noise into the oscillator passband as the primary limitation on achievable spectrometer sensitivity. We have made the first reported routine use of NMR thermometry techniques for calibration of cryostate thermometers. Mr. Murphy has begun the assembly of a self-locked nuclear resonance thermometer. Initially, we will use $KClO_3$, but are examining $NaBrO_3$ and $CrBr_3$ as interesting alternate materials.

5.5 Studies of Amorphous Semiconductors

Personnel: R. C. Walleigh, S. D. Senturia, C. R. Hewes

Sponsorship: Office of Naval Research

We have extended our earlier measurements of the frequency dependence of the conductivity of a memory-type chalcogenide glass up to 100 MHz. The behavior observed is characteristic of band conduction.

6.0 Microelectronics and Silicon Device Technology

Personnel: D. L. Smythe; D. M. Chapman, G. K. Montress, R. C. Busby

Sponsorship: Advanced Research Projects Agency

A program has been started with the objective of providing the device designer with an accurate way to predict junction breakdown voltages in silicon diffused junctions, where breakdown is dominated by crowding of the electric field at the curved junction surface. Preliminary results indicate that the breakdown voltage is highly correlated with the impurity gradient at the metallurgical junction. More theoretical and experimental work is being done to check this observation. Repeatibility has been a problem.

We are also investigating the reduction of the electric field at the junction surface by using a field plate which induces a field in the oxide around the junction. Although it is known that a field plate will increase the breakdown voltage of a diffused junction, the amount

of increase is at present not known except for the few specific devices which have been fabricated. The theoretical relationships need to be worked out. This work should also be applicable to Schottky barrier diodes.

7.0 Electric Propulsion

Personnel: R. D. Thornton; W. W. Carson, W. S. Brown, D. Saar
Sponsorship: National Air Pollution Control Administration; Department of Transportation, and M. I. T. Funds

The M. I. T. hybrid electric car was substantially modified. A new permanent magnet alternator was built using hard ferrites and a heat-shrink technique to prevent mechanical failure of the magnets. Based upon experiences with this machine a new one is being planned that will give substantially higher power output per pound than is obtained with similar-sized, more conventional machines. The hope is to eventually replace the ferrite magnets with the newer high energy rare-earth magnets. Work was started on contructing high-power-density lead-acid batteries for hybrid vehicles. A bipolar construction has been used, and it shows a potential factor-of-three increase in peak power output with no decrease in energy storage capability. Current efforts are directed toward experiments with different materials, such as titanium, which will provide reasonable life when used as the barriers between cells. The work on the electronic two-phase speed controller was finished and used successfully for sustained driving under a variety of conditions.

S. Marshall completed his thesis on "Linear Synchronous Motors for Transportation", and demonstrated a model that verified the analysis. The motor concept has practical possibilities, but further work is needed to obtain a fair comparison with other possibilities for propulsion for high speed trains and lower speed transit systems.

8.0 High Power Solid State Devices

Personnel: R. D. Thornton; R. Blanchard, M. Timko
Sponsorship: Advanced Research Projects Agency

Mr. Blanchard completed a thesis on "A Power Transistor with an Integrated Thermal Feedback Mechanism". He extended the work of Borky

and was able to fabricate a power transistor incorporating the principles of thermal feedback. The device had good electrical properties, but further work is needed to assess the effectiveness of the thermal feedback for second breakdown prevention. M. Timko completed a thesis which explored the possibility of using integrated circuit technology to fabricate improved gate-turn-off controlled rectifiers. He tried two methods of incorporating gate turn off amplification within the device, and was able to build devices using these principles. The most promising technique seemed to be an interdigital structure with special attention to the dimensions and diffusion profile. The thesis contains derivations of some of the limits of performance that can be expected.

9.0 Study of Basic Device Parameters in the Lead Salts

Personnel: R. H. Rediker, J. N. Walpole; R. Guldi, F. Leonberger, H. St-Onge

Sponsorship: Office of Naval Research, National Science Foundation Traineeship

Our research program in lead and lead-tin chalcogenides continues in three areas of work. These are (1) radioactive tracer diffusion, (2) metal-semiconductor barriers, and (3) high electric field studies. The principal aim of all three areas is better knowledge of fundamental properties of these materials in order to improve the performance of devices and to make possible new devices.

9.1 Radioactive Tracer Diffusion

This investigation is concerned with establishing a more complete model for the diffusion processes and the defect mechanisms in PbSe. We are obtaining and analyzing data on the diffusion of both radioactive lead and radioactive selenium tracers in PbSe and interpreting these data in the light of our previous theoretical and experimental investigation of interdiffusion, using p-n junction depth penetration techniques.

We have measured the tracer diffusion constant for Se-75 in both n and p-type PbSe at 700°C and at 800°C and have found significantly lower values of the diffusion constant than have previously been reported. We have also found that the diffusion of Se-75 proceeds slightly faster in Se-saturated

(p-type) PbSe than in Pb-saturated (n-type) PbSe. Further measurements of the tracer diffusion constant of Se-75 at other temperatures and diffusion conditions are being made, and measurements of the tracer diffusion constant of Pb-210 at various temperatures and diffusion conditions are being initiated.

9.2 Metal-Semiconductor Barriers

In close collaboration with K. W. Nill, A. R. Calawa and T. C. Harman of Lincoln Laboratory, we have continued our work on metal-semiconductor barriers on PbTe and $Pb_{1-x}Sn_xTe$. We have shown, using a number of different metal contacts on n and p-PbTe, that the barrier height is not determined by surface properties, as for many semiconductors, but rather it varies as one would predict from the value of the metal work function. The Fermi level at the interface is not pinned within the forbidden gap and, in fact, low work function metals on p-type material produce strongly inverted surfaces. The properties of the inverted surface are being studied further.

These barriers have also been studied as devices. Because of the inverted surface, laser action is possible. We have reported the observation of laser action from the metal-semiconductor contacts on PbTe and $Pb_xSn_{1-x}Te$ for x as large as 0.28 corresponding to a wavelength of 28.9 μm. The observed threshold currents required for laser action are comparable to the lowest threshold p-n junction lasers. The low thresholds may be a direct result of the evaporated metal barrier which both confines the optical cavity and permits efficient heat transfer from the junction.

9.3 High Field Conduction Processes

We are investigating two regions of the field-dependent conductivity for homogeneous bulk samples of the Pb salts. These are the hot-electron region where the velocity distribution of the carriers is significantly perturbed from a thermal one and the avalanche multiplication region in which the density of carriers increases by ionization across the energy gap.

Nanosecond pulse techniques are used to measure the current-voltage characteristics of bulk samples of n-type PbTe and n-type PbSe at 77°K and 4.2°K for carrier concentrations ranging from 1×10^{17} cm^{-3} to 5×10^{17} cm^{-3}. Samples of cross sections to typically 60×10^{-6} cm^2 and lengths of typically 0.5 mm are required in order to reach drift velocities near 10^7 cm/sec, where appreciable carrier heating occurs. The samples are made either in parallelepiped or dumbbell shapes. Velocity-field characteristics are obtained by geometrical considerations and are believed to be accurate to 15%.

We have observed deviations from ohmic conduction at fields of few hundred volts/cm, the drift velocity showing a clear tendency towards saturation. A decrease in mobility is observed up to about 1000 V/cm and 2500 V/cm for PbTe and PbSe respectively, where an inflection point occurs in the curves. This current runaway is consistent with the occurrence of avalanche multiplication. If a comparison is made with InSb where multiplication sets in at about 230 V/cm, it is striking that the region of saturating velocity extends to much higher electric fields in the Pb salts. This behavior is consistent with a much stronger coupling to polar optical models in the Pb salts. We have performed a theoretical investigation which indicates that in the lead salts polar optical scattering is dominant at high fields. This investigation shows that nonpolar optical scattering can be neglected but that the effects of the strong nonparabolicity of the energy bands are important at high fields.

In PbTe at 77°K an instability was observed with a threshold field of 1040 V/cm for all samples. This instability appears to be a bulk property and is polarity independent. In order to get a better understanding of this instability, a pulsing system of low characteristic impedance has been constructed and will be used to measure the velocity field characteristics.

A similar instability has been observed in mixed crystals of (PbSn)Te. Preliminary results indicate that the threshold of the instability is a function of the energy gap.

10.0 Photoluminescence and Photoconductivity in Semiconductors

Personnel: R. H. Rediker, J. S. Moore; A. Hartman

Sponsorship: Air Force Office of Scientific Research

Photoluminescence from silicon and germanium at $3^{\circ}K$ has been found to be a strong function of electric field in the crystal. Quenching of certain strong lines in the spectra has been achieved for electric fields of less than 10 V/cm in silicon and less than 3 V/cm in germanium. The modulation of an emission line arises from the dissociation of the electronic complex associated with the emission. The electronic complexes studied are the exciton (a mutually bound electron and hole), the bound exciton (an exciton bound to a neutral donor or acceptor impurity) and the molecular exciton (a loosely coupled exciton pair). These complexes have low binding energies and thus may be dissociated in collisions with electrons and holes. The luminescence lines associated with the molecular and bound exciton are quenched by the electric field, while the luminescence from the free exciton is at first enhanced and then for higher fields is quenched. These results are described in terms of the electric field dependent continuity equations for the molecular exciton and bound exciton. For small electric fields the rate of dissociation of the complexes is proportional to the power delivered to the charge carrier populations by the electric field. Also, the enhancement of the free exciton luminescence results from the dissociation of the bound and molecular excitons since their dissociation represents free exciton generation mechanisms which are not present in the absence of the electric field.

In photoconductivity measurements in germanium at $3^{\circ}K$, a new negative differential conductance phenomenon has been discovered. The current-electric field characteristics of germanium samples, subjected to uniform photo-injection of charge carriers, reveal a current controlled negative differential conductance region. The breakdown field for the negative conductance is approximately 1 V/cm and increases as the rate of photo-

injection is increased. Associated with the negative differential conductance is a strong quenching of the molecular exciton luminescence. The increase in the conductivity of the sample results from either an increase in the mobility of the charge carriers or an increase in their concentration. An increase in mobility is expected, since for the low temperature and the large density of molecular excitons of the measurement, the charge carrier mobility for prebreakdown fields should be reduced by scattering with molecular excitons. The molecular exciton concentration and thus the concentration of scattering centers are reduced after breakdown as is indicated by the quenching of the molecular exciton luminescence. The increase in breakdown field with increased photo-injection is also expected with this model, since the increase in molecular exciton concentration should result in a decrease in charge carrier mobility.

In another experiment to observe enhanced band edge absorption caused by the generation of momentum-conserving phonons at a tunnel junction, no modulation of the absorption edge was observed. This result implies that the lifetime of the large-wavevector TO phonons is less than 10^{-7} sec at $3^{\circ}K$ in silicon tunnel diodes.

Negative extrinsic photoconductivity in cobalt-doped silicon at room temperature has been studied. To further understand this phenomenon, measurements have been made of the temperature dependence of resistivity and Hall coefficient for this material. The impurity levels associated with the cobalt have been shown to be a donor level 0.40eV from the valance band and an accepter level 0.53eV from the conduction band. These levels appear to be due to different charge states of the same center. These determinations are supported by absorption data and are consistent with our explanation of the negative photoconductivity.

11.0 Study of Stannic Oxide as a High Temperature Semiconductor

Personnel: R. H. Rediker, A. Linz, C. G. Fonstad, T. Credelle

Sponsorship: Air Force Office of Scientific Research, Advanced Research Projects Agency, National Science Foundation Traineeship

11.1 Crystal Growth

Work has continued on improving the stannic oxide crystal growing system and it has been used to grow a collection of high quality crystals with differing room temperature carrier concentrations. The growth technique used is a low pressure, inert carrier-gas free, chemical vapor deposition technique based on the reaction:

$$SnCl_4(g) + 2H_2(g) + O_2(g) \overset{\Delta}{\rightleftarrows} SnO_2(s) + 4HCl(g)$$

It is a continuously flowing system and it offers wide flexibility and extreme control over the reactants and over the growth reaction itself; it has been described in the literature. The crystals produced have been of higher purity and have had much higher low temperature mobilities than any previously available stannic oxide. Antimony doped, and not intentionally doped crystals have been grown.

The feasibility of seeded growth has been demonstrated. The growth on seeds shows many reentrant faces, however, due to turbulence in the gas flows, a common occurrence in vapor phase systems that is receiving further attention. Additional objectives of the crystal growth program will be epitaxial growth on prepared substrates, and introducing electronic dopants other than antimony.

11.2 Electrical Properties

The procedure for fabricating Schottky barriers on n-type stannic oxide has been perfected, and these devices have been used extensively to measure the net donor concentration, N_d, of samples. A valuable technique for determining the homogeneity of the donor concentration across a sample by using closely spaced 2 mil diameter barriers has been developed. Such information is essential when one is studying a new semiconductor where the

growth is not under complete control and inhomogeneities should be anticipated. Larger diameter, 20 mil, barriers have been used to measure N_d for comparison with N_d measured from Hall effect measurements. The close agreement found indicates that shallow trapping is not important in these crystals and $\mu_H \simeq \mu_d$.

The conductivity anisotropy in SnO_2 has been found to be small, ≤ 1.2 at 77°K and 297°K. Measurements of n, μ_H, and σ have been made between 20°K and 625°K on n-type bars oriented in the a-direction. The room temperature carrier concentrations of the samples range from 7×10^{15} cm^{-3} to 2×10^{18} cm^{-3}. A donor level due to antimony is seen 37 meV below the band edge and a second level ascribed to oxygen vacancies is seen 140 meV below the edge. A polaron effective mass of 0.39 m_e was found consistently in all of the analyses. Polar optical-mode scattering, deformation potential scattering, and ionized impurity scattering have been used to explain the mobility and excellent agreement is found between the theories and the experimental data. Above 250°K polar optical mode scattering with a characteristic temperature of 1080°K is dominant; below 250°K acoustic deformation potential scattering with $E_{IC} \simeq 8$ eV is important; and at the very low temperature ionized impurity scattering is important in all samples. In the purest samples a peak Hall mobility over 13,500 cm^2/V-sec is measured at 40-50°K.

Above 625°K (~350°C) it was found that irreversible changes occurred in the electrical properties of the stannic oxide samples. It is felt that both the sample holder materials and the atmosphere in the holder contributed to that change. The determination of what materials and atmospheres can be used with stannic oxide above 350°C will be very important and is being considered.

11.3 Optical Absorption Edge

Measurements of the optical absorption edge have been made between 5°K and 297°K on undoped, oriented stannic oxide samples using polarized light. For light polarized E⊥c, exciton structure below 80°K and an Urbach's rule broadened direct allowed transition edge above 80°K are both seen similar to

the observations of Nagasawa and Shionoya. A minimum bandgap of 3.6 eV at $0^{o}K$ and a separation of 0.12 eV between two split valence bands is seen. Our measurements for light polarized E||c are the first ever reported on high mobility SnO_2 and they are the first experimental support of Nagasawa's prediction that the transitions from the two valence bands are direct forbidden for E||c. A plot of (absorption coefficient)$^{2/3}$ vs. photon energy for E||c yields two linear regions corresponding to the two transitions and giving band energies consistent with the E⊥c observations. The shift of the bandgap with temperature can be seen in this polarization, E||c, and the first measurement of the room temperature bandgap minimum, 3.45 eV, can be made. The separation of the valence bands remains 0.12 eV.

The photoresponse of Schottky barriers has also been studied and found to be consistent with the above observations.

12.0 Investigation of the AlGaAs-GaAs System

Personnel: R. H. Rediker; W. H. Berninger; R. J. Lafond, J. F. Womac

Sponsorship: Advanced Research Projects Agency,
Air Force Office of Scientific Research

Liquid phase epitaxy has been used to deposit tin, tellurium and zinc doped layers of $Al_xGa_{1-x}As$ on the {111B} and {100} faces of GaAs substrates. Photoluminescence and photoreflectance measurements have been made on layers of various carrier concentrations and alloy compositions. In particular, the direct gap, its spin orbit split component and the first two ultraviolet reflectivity peaks have been determined as a function of x for $0 < x < .7$ by photoreflectance for samples of carrier concentration on the order of 10^{17} cm^{-3} at room temperature. This technique has been used to examine the direct edge of high purity GaAs at $77^{o}K$ where structure attributed to coulomb screening of the free exciton is observed as a function of carrier concentration and incident light intensity. Photoluminescence of Sn doped material shows that for $x < .35$, where the bandgap of the alloy is

known to correspond to direct transitions, the emission spectrum is qualitatively similar to that of GaAs. The results for higher Al concentration indirect gap samples are being evaluated.

The influence of growth conditions on the electrical characteristics of tin doped n-n heterojunctions of $Al_xGa_{1-x}As$-GaAs has also been investigated. By varying the growth conditions, both ohmic and rectifying characteristics have been obtained. These results can be explained in terms of grading of the Al and Ga concentrations about the interface which is consistent with the growth kinetics and the AlGaAs ternary phase diagram. Although it should be possible to grow rectifying junctions at any temperature by suitable adjustment of the melt composition, only junctions grown below 850°C have exhibited rectification.

Assuming the entire bandgap discontinuity is the conduction band, these results can still be explained using a model similar to that of Oldham and Milnes [Solid-State Electronics 6, 121 (1963)] for a graded gap n-n heterojunction. If the grading is comparable to a quantity proportional to $L_D x\sqrt{\Delta\chi/kT}$, where L_D is the extrinsic Debye length [$L_D^2 = kT\varepsilon/q^2N_D$], the solution to Poisson's equation shows that, in fact, there will be a negligible barrier in the conduction band. We have expanded Oldham and Milnes' model to include externally applied bias and variations in doping and effective mass through the heterojunction and have thus been able to explain our results. Specifically, our results indicate that, with the entire bandgap discontinuity in the conduction band, the ohmic heterojunctions are graded to the order of 200 Å for an N_D of 10^{18} carriers per cc.

The energy variation of the E_1 ultraviolet reflectivity peak has been studied as a function of alloy composition over the range $0 < x < .7$. This technique has been exploited as a nondestructive technique for the determination of alloy composition.

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Section 6.0

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Sections 7.0 and 8.0

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S. G. Marshall, "Linear Synchronous Motors for Transportation", S.M. Thesis, Department of Electrical Engineering, February 1970

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C. G. Fonstad, "Stannic Oxide-Crystal Growth and Electrical Properties" PhD, Department of Electrical Engineering, September 1970

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III. LOW-MOBILITY AND AMORPHOUS SEMICONDUCTORS

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Sponsorship:

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Research Report

1.0 Low-Mobility Semiconductors

Personnel: David Adler, Ulrich Birkholz

Sponsorship: Advanced Research Projects Agency, Office of Naval Research, Max Kade Foundation

1.1 Optical And Electrical Properties

It has long been a mystery why many transition-metal compounds have optical spectra suggestive of extremely localized d electrons, while electrical

transport studies suggest that ordinary electronic conduction occurs in relatively wide (1-5eV) bands. For Mott insulators, these results can be understood only if correlations are explicitly taken into account, for otherwise the material will appear to be metallic. But, furthermore, the d bands often appear to be very near the atomic limit, since the localized crystalline-field excitations (Frenkel excitons) are neither broadened nor shifted from those of the isolated ion in a similiar environment. In highly ionic materials such as the transition-metal oxides and halides, it is thus extremely difficult to explain the lack of observation of thermally activated hopping conduction. A simple resolution of this puzzle has previously been suggested; i.e. the predominant electrical conductivity in p-type semiconductors can occur in the highest filled band associated with the anions. Carriers in such bands can be expected to have relatively low effective masses and move with a higher mobility than holes which must hop from cation to cation. Nevertheless, they will not dominate the conductivity unless a sufficient carrier concentration can be excited. Experimentally, however, it appears from both optical and photoemmission studies that the anion bands are often well below the highest filled d state in energy, even in materials in which band-like hole conduction has been unambiguously shown to predominate.

A theoretical analysis of the energy band structure of some insulating transition-metal oxides, based on the Hubbard model for treating electronic correlations, has been carried out. It is indeed found, in agreement with the experimental data, that the oxygen 2p band is 2-4 eV below the highest filled cation.d levels. However, when correlations are important, it cannot be concluded from these results that electrical conduction does not take place in the 2p band. The reason for this is that the electrical properties are always studied on doped or non-stoichiometric materials, and the relative positions of the d and 2p bands can be shifted by as much as several eV by the introduction of a minority valence state of the transition-metal ions. When the extrinsic energy-band structure is calculated, this energy shift becomes obvious. Excellent agreement with the experimental electrical and optical properties for the cases of NiO and CoO have been obtained by this method of estimating the intrinsic and extrinsic band structure. An alternative description of the final result is that heterovalent impurities or non-stoichiometry splits off a part of the anion p band and raises it sufficiently close to the Fermi level that hole conduction in this sub-band can dominate the electrical transport. Analogous results in n-type material can be obtained, although in this case conduction occurs in the lowest unfilled s band of the cations. An important corollary of this work is that no conclusion about the nature of the electrical transport in Mott insulators

should be made from the optical data alone. This arises because optical spectra are dominated by intrinsic processes and transport data by extrinsic processes, and in highly correlated systems the relative energies of these processes are not simply related.

1.2 Small and Large Polarons in NiO

NiO is always a partly compensated, p-type semiconductor, which has never been made degenerate, neither by doping nor by application of high pressure. The dc transport results point to band-like conduction in a relatively wide valence band. On the other hand, ac conductivity experiments imply that very localized, bound carriers conduct by hopping, even at very low temperatures.

Since the material is 96% ionic, it can be expected that polaron states represent a better starting point for a theoretical analysis than electron states. The dc transport data have been interpreted in terms of large-polaron theory. A detailed analysis leads to the conclusion that free holes form large polarons of a radius equal to about two interatomic spacings, and move in a valence band with an effective mass of 6 free electron masses. The electron-phonon coupling constant, α, is about 3, indicative of intermediate coupling. The reason for the small polaron radius in NiO is the stiffness of the lattice not the strength of the coupling. With the above parameters, the experimental mobility vs. temperature curve can be derived with high precision.

The ac conductivity data have been interpreted by means of a generalization of small-polaron theory. In order to account for the enormously long staying time and the observation of hopping conduction at low-temperatures, it must be assumed that the effective overlap integral between adjacent $3d^8$ states is of the order of 0.01 eV. This is an order of magnitude lower than the APW calculations indicate, and can be justified only in terms of a large correlation narrowing . Rederivation of small-polaron theory in terms of low effective overlap integral then predicts a small activation energy for hopping and a low transition temperature for the predominance of hopping over band conduction, both results in accord with experiment.

The vastly differing overlap integrals necessary to explain the free and bound carrier transport properties are consistent with a previously suggested model in which these carriers move in different bands.

1.3 Band Sructure of Insulators

When correlations are important, ordinary one-electron theory is inadequate for a quantitative analysis of the electronic energy-band structure. On the other hand a model which begins with the isolated ionic energy levels, takes into account the effects of crystal environment, and introduces overlap effects as a perturbation at the end can give an excellent representation of the elementary excitations of the material, since the correlations are automatically built into the calculation. Using an experimental method for obtaining the effects of polarization, covalency, and screening on the free-ion levels, and assuming a symmetric spread to the quasiparticle bands as indicated by the Hubbard model, we have estimated the energy-band structures of MgO, TiO_2, and NiO. In each case, the derived structure is in agreement with the optical data. A method of representing the band structure in terms of an effective one-electron quasiparticle diagram has been presented, although the rules necessary to properly interpret such a diagram are formidable.

1.4 Correlations in Narrow Energy Bands

In Mott insulators such as NiO and MnO, the d electrons appear to be quite near the ionic limit of narrow-energy-band theory. In such a case, Luttinger's theorem that the Fermi surface volume remains invariant in the presence of electronic interaction clearly is invalid, due to divergence of the perturbation expansion on which its proof is based. Near the ionic limit, it might be expected that a perturbation expansion around zero bandwidth is more applicable. The electrical conductivity has been calculated in the strong-correlation limit, to first order in the ratio of the bandwidth to the intraionic coulomb repulsion. The ordinary band-like equations do not remain valid even in first order, and a renormalized effective mass must be used. The derived expression has been used to evaluate the contribution of holes in the $3d^8$ band to free carrier conductivity in NiO. It is concluded that this contribution can be quite small, and is perhaps dominated by 2p band conduction, even if the $3d^8$ band is above the top of the oxygen 2p band.

1.5 Metal-Nonmetal Transitions

A general scheme for classifying the conductivity anomalies usually generically referred to as metal-nonmetal transitions has been proposed. A sharp distinction is made between transitions that occur under equilibrium conditions and those that exist only when equilibrium is destroyed, as when an external electromagnetic field is applied to the material. The equilibrium transitions, which are induced by a variation in either pressure,

temperature, or carrier concentration, can be due to an overlap of two energy bands, an instability of the metallic state at low temperatures towards a lowering of crystal symmetry, or a Mott transition. An analysis of the available data has been used to classify the many transitions that have been observed as to their most likely origin.

1.6 Insulator-Metal Transition in $FeSi_2$

The nature of the $FeSi_2$ phase transition, which occurs near 1200K, has been studied by electrical, magnetic, optical, and thermal measurements. The high-temperature phase, α-$FeSi_2$, has a tetragonal structure with 3 atoms per primitive cell; the low-temperature phase, β-$FeSi_2$ has orthorhombic symmetry with 48 atoms per primitive cell. Below the transition temperature, β-$FeSi_2$ is an intrinsic semiconductor (Eg=0.85eV), whereas above the transition, α-$FeSi_2$ exhibits metallic conduction, essentially independent of temperature. These results have been confirmed by thermoelectric and thermal conductivity measurements. In addition, it has been determined that β-$FeSi_2$ is diamagnetic below 650K. Both α-$FeSi_2$ and β-$FeSi_2$ show unusual increases of paramagnetic susc ptibility with increasing temperature. Reflectivity experiments on α-$FeSi_2$ indicate only free carrier absorption, whereas β-$FeSi_2$ exhibits an absorption edge and a reststrahlen band. A Kramers-Kronig analysis gives a large dielectric constant, ε=62. The energy gap and dielectric constant are not consistent with either a band overlap or an excitonic insulator transition. The magnetic data do not suggest that a Mott transition occurs. Rather the experimental results can be explained using the crystalline-distortion model proposed by Adler and Brooks. At the transition there is a pairing of the cations in $FeSi_2$ along a given crystalline axis, which causes a splitting of the 3d band. A tentative band-structure model has been proposed for both phases which accounts not only for the insulator-metal transition, but also for the detailed electrical and optical properties of doped β-$FeSi_2$, which indicate the predominance of small-polaron conduction in n-type material and of band-like conduction in p-type material. This can be explained by the assumption that hole conduction occurs in the 3p band of the Si, the lower of the distortion-split 3d bands being depressed below the top of the 3p band.

2.0 Amorphous Semiconductors

Personnel: David Adler, Floyd O. Arntz, Ulrich Birkholz, Kathryn B. Kanarek, Richard Ku, Bimal P. Mathur, Donnie K. Reinhard

Sponsorship: Advanced Research Projects Agency, Army Research Office-Durham

2.1 Band Structure of Amorphous Semiconductors

A qualitative procedure for taking into account the effects of electronic correlations and electron-phonon interactions in the band tails of amorphous semiconductors has been proposed. The resulting quasiparticle spectrum has many of the same features as appear in the simple one-electron approximation, but two important modifications must be introduced. Because of correlations, the localized states in the valence-band tail are split in two, double occupancy costing an energy of the order of tenths of an eV. On the other hand, localized states in the conduction-band tail are also effectively increased in energy relative to the valence-band mobility edge, so that the redistribution of electronic states in highly disordered systems such as the chalcogenide glasses can take place much as Cohen, Fritzsche, and Olvshinsky postulated. The effects of the electron-phonon interaction are such as to partially compensate for correlation effects, since ionic distortions around localized electrons tend to reduce their energies relative to those of delocalized states.

2.2 Thermal Breakdown in Amorphous Semiconducting Films

A model for thermal switching in films of chalcogenide and oxide glasses is being investigated, explicitly taking into account both radial and axial heat flow, the filamentary nature of the conducting path, and the field dependence of the conductivity resulting from non-ohmic electronic effects. Preliminary results indicate a small temperature rise prior to breakdown, but a large threshold field in the thinner films, a very hot central filament, and an environment that cools considerably after switching.

2.3 Composition Dependence of Switching Parameters

The effects on the switching parameters of substituting Se for Te in some memory-type chalcogenide glasses have been systematically investigated. In particular, the system $As_4Ge_{16}(Te_{1-x}Se_x)_{80}$ has been studied in detail. The glass with x=0 had previously been shown to be an excellent memory-type material, the switching being completely reversible and the conducting state resulting primarily from regions of As-doped polycrystalline Te. Except for the region near x=1/2, no difficulty in producing homogeneous bulk glasses was encountered. However, good memory switching was obtained only near x=0. The region $0.1<x<0.3$ provided threshold switching with an increasing threshold voltage and relatively poor dc stability. The material could be therm-

ally crystallized via an annealing technique, but was then quite inhomogeneous and possessed a resistivity two orders of magnitude higher than the x=0 ON state. For x>0.6, the threshold field had increased sufficiently so that no electrical switching was obtained up to 400V. These results are consistent with the hypothesis that doped, crystalline Te is primarily responsible for the ON memory state. Since Se is a wide gap semiconductor and has a much higher crystallization temperature than Te, substitution of Se for Te should indeed have deleterious effects on the switching process.

2.4 Experimental Studies of Thin-Film Switching

Experimental studies of the influence of electron bombardment and dynamic strain on switching in amorphous chalcogenide films will soon be underway. Equipment and r.f. sputtering techniques have been developed for the production of films for these studies. Memory switching films have been produced and threshold switches, upon which the above studies shall be concentrating, are anticipated shortly.

Films tested to date exhibit voltage oscillations prior to formation of the memory state when a large series resistance is employed. Evidently capacitance is essential for the appearance of these oscillations. We are convinced regions of the film, coupled thermally and electrically, cannot account for the observed oscillations unless one includes stray capacitance or space-change effects. Evidently the necessary inductive component is due to thermal lag in the bulk of the amorphous film and the influence of resistive components present in the circuit is cancelled by the negative differential conductance of a filamentary conducting region.

2.5 Effective Charge of Ions in Chalcogenide Glasses

The Te^{125} magnetic resonance experiments carried out on amorphous and polycrystalline TeGe alloys has been compared with similar measurements on PbTe and SnTe in order to obtain an estimate of the effective charge on Te ions in the amorphous chalcogenides. It was concluded that the effective charge of a Te atom with two Te nearest neighbors is close to zero, that of a Te atom with one nearest-neighboring Ge atom is -0.18e, and that of a Te atom with two nearest-neighboring Ge atoms is -0.35e. Thus, the relatively small effective charges in the chalcogenide glasses make it unlikely that a field-induced ferroelectric-type displacement can account for the observed switching properties.

2.6 Properties of Crystalline and Amorphous Si_2Te_3

A program to determine and compare the properties of crystalline and amorphous Si_2Te_3 has been initiated. Si_2Te_3 is the only compound in the Si-Te system. Single crystals have been prepared by vacuum sublimation in a temperature gradiant near 750C; the crystals are red transparent platelets, of thickness between 50 μm and 1000 μm. Optical absorption has been measured between 0.5 μm and 10 μm, indicating that the optical gap is near 2 eV. The gap exhibits a blue shift of about 1 meV/K as the temperature is reduced. Photoluminescence has also been measured, and a broad peak near 1.3 eV has been observed. No luminescence appears in the vicinity of the optical gap. This is consistent with observations on arsenic chalcogenides. A study of the corresponding properties of rf sputtered amorphous Si_2Te_3 films is being carried out.

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IV. MICROWAVE AND QUANTUM MAGNETICS GROUP

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Sponsorship:

* Advanced Research Project Agency SD-90/DAHC 15 67C 0222, DSR 75113/72213, 75116/72216;
Advanced Research Process Agency, DAHC 15 70C 0190, DSR 72144;

Research Report

1.0 Resonance Losses in Garnets

Personnel: D. J. Epstein, L. Tocci

Our investigation of microwave resonance losses in silicon doped yttrium-iron garnet (Si-YIG) is nearing completion. The results will appear in a doctoral thesis document being written by Mr. L. Tocci, who has carried out microwave resonance experiments on Si-YIG as a function of composition, frequency and temperature. An anomalous loss peak occurring in the temperature interval 300-500°K has been identified with a four-level model for valence-exchange loss. The linewidth anisotropy, change in effective field and the dynamic contribution to the first order anisotropy constant have been examined in detail and close agreement with the model is obtained. The energy parameters which characterize the model have been determined. Surprisingly, the activation energy for magnetic loss is found to be appreciably larger than that for electric conduction. This unanticipated result turns out to be consistent with earlier transport studies which suggest that conduction in Si-YIG occurs via a band and not by electron hopping as previously believed. An energy level diagram has been formulated which accounts very nicely for the difference in magnetic and electric activation energies.

2.0 Non-linear Conduction in Si-YIG

Personnel: D. J. Epstein, D. C. Bullock

Negative resistance phenomena, similar to those widely reported for semiconducting glasses, have been seen in a variety of polycrystalline oxide films. Quite recently, negative resistance effects have been found in single crystal wafers of Cu_2O and NiO and a memory effect has also been seen in these crystals. We have discovered the occurrence of a negative resistance and conductive memory state in Si-YIG. Although YIG is well known as a magnetic material having extremely desirable microwave properties, it has, until now, not been known to possess features that would also make it attractive in semiconductor applications.

Conductive measurements on thin wafers (approximately 1 mil thick) of Si-YIG, coated with ohmic contacts, exhibit a current controlled negative resistance capable of sustaining oscillations at frequencies up to 1 MHz.

For voltages exceeding a critical threshold the sample enters a conductive memory state. We have been successful in repeatedly cycling samples into and out of the memory state. However, as yet no systematic tests of repeatability lifetime have been made.

3.0 Growth of Magnetic Crystals

Personnel: J. T. Carlo, R. C. Folweiler, D. Gabbe, R. L. Gentilman

Two crystal growth efforts are in progress: one devoted to the growth of bulk single crystal YIG by the top-seeded solution method (TSS); the other a program to grow thin film YIG by the chemical vapor deposition (CVD) procedure.

The several crystals that we have thus far grown by the TSS method show an excessive number of cracks and inclusions. A microprobe analysis revealed that the inclusions have the YIG-hematite eutectic composition. We have found that growth, once inibiated, proceeds very rapidly, a phenomenon which suggests that crystallization is occurring from a supercooled liquid. Crystallization under such conditions would account for the observed inclusions and for the tendency of the crystal to develop strain cracks. We are currently building a three zone platinum-wound furnace that will enable us to modify the thermal gradients in the growth zone so that we can enhance convective flows and, thereby, reduce supercooling.

In our program to grow epitaxial films of yttrium-iron garnet (YIG) by the CVD method we have completed several major modifications in our basic apparatus, including: a new chlorinating generator and gas injector design; replacement of the Kanthal wound furnace with a more versatile globar heated furnace; improvement of the cold traps and furnace tube-end seals, and the addition of a solid-particle trap.

With these modifications we have been able to achieve a set of flow conditions which lead to the production of fine particle YIG. We are now modifying flows in an effort to create conditions under which the YIG reaction will occur on the furnace walls rather than in the vapor. A subsequent step will be the introduction of an appropriate substrate for epitaxial growth.

4.0 Phonon and Photon Pumped Nuclear Spinwaves in the Antiferromagnet $RbMnF_3$

Personnel: F. R. Morgenthaler, A. Platzker

Dr. A. Platzker has completed his doctoral research on phonon- and

photon-pumped electronic and nuclear spinwaves in $RbMnF_3$. General linear and nonlinear excitation of spin wave modes in cubic antiferromagnets which also carry nuclear magnetic moments have been investigated theoretically and experimentally. The theory is applicable to both photon and phonon pumping but the experiments, performed on single crystal $RbMnF_3$ were confined to the more efficient and versatile phonon excitation which was used to explore nuclear spin waves.

Major results include a method for calculating nonlinear spin wave instabilities of any order in magnetic materials with any number of sublattices. As an illustration, the theory was applied to general first order nonlinear processes in an isotropic ferromagnet before being used to investigate the numerous first order instability processes in the flopped cubic antiferromagnet.

The first observations were made of nonlinear magnon induced nuclear spin wave instabilities in any antiferromagnet. The experiments were carried out on $RbMnF_3$ with a longitudinal phonon beam propagating parallel (or nearly so) to the sublattice magnetizations in the flopped configuration. Nuclear relaxation rates were obtained as a function of the magnon frequencies and wave vectors.

5.0 Frequency and Mode Conversion of Velocity Modulated Magnetoelastic Waves

Personnel: F. R. Morgenthaler, H. L. Hu

The frequency of a magnetoelastic wave propagating in a ferromagnet can be altered by a suitable time variation of the bias magnetic field and the character of the wave can be converted from magnon-like to phonon-like (or vice versa) by suitable time and/or space variation of the bias field; such frequency and/or mode conversion can be utilized in fundamental spectroscopy as well as for microwave ultrasonic devices.

H. Hu is continuing his doctoral studies which use an infrared laser to study Bragg scattering from magnetoelastic wave packets in single crystal YIG. This work is aimed at clarifying the mechanics of space and time conversion, in particular, the role of defocussing fields in a nonuniform medium.

6.0 Coupling of Magnetoelastic and Electromagnetic Waves

Personnel: F. R. Morgenthaler, J. Doane

J. Doane has completed a doctoral thesis aimed at improving our understanding of the mechanisms of coupling between electromagnetic energy and magnetoelastic energy in delay lines, with the hope of developing better excitation schemes. The theory involves analytic solutions of linear ordinary differential equations with variable coefficients.

A systematic procedure has been developed for finding exact solutions of certain differential equations of arbitrary order describing reflection and transmission of waves in media with a bounded region of inhomogeneity. This procedure involves solution by generalized hypergeometric functions. It has been applied to find reflection coefficients for spin wave conversion at a fourth order turning point near which the static magnetic field varies monotonically. Solution for a variation with a single valley has also been outlined. A "source equation" method has been described which allows a broader class of differential equations to be solved exactly using the above procedure. This method has been applied to a fourth order equation to find the reflections and transmission efficiencies at a magnetoelastic crossover point. Comparison with previous solutions shows that successive approximations schemes are not reliable for calculating reflections. Coupled second order equations are derived and combined into one sixth order equation simultaneously describing interactions between "magnetostatic", "exchange," and elastic waves in the presence of both a turning point and a crossover point. An expression for the overall conversion efficiency is found in terms of sines of complex arguments.

Hypergeometric functions can also be used to solve certain coupled mode problems in which reflections are neglected. Here they are used to find analytic expressions for conversion efficiencies at a magnetoelastic coupling point. Previous solutions required successive approximations or numerical integration. Solutions for the reflections on certain nonuniform transmission lines are also described.

7.0 Magnetostatic Surface Waves

Personnel: F. R. Morgenthaler, J. K. Jao

The characteristics of TE surface waves propagating in an obliquely magnetized uniform ferrite medium have been examined -- with special emphasis given to the magnetostatic region of the dispersion relation. It appears that independent control of the propagation and decay constants is possible. In addition, the waves are nonreciprocal in the field displacement sense allowing novel magnetic control to be exercised over them. Moreover,

magnetic control of the net exchange torque acting upon a long wavelength surface spinwave as well as its penetration depth is possible because changes in the magnetic field orientation can alter the dipolar interaction which in turn modified the value of $\nabla^2\bar{m}$. It should therefore be possible to vary the effective exchange constant of certain surface waves -- allowing the exchange curvature of the dispersion relation and hence group velocity of the waves to be controlled. Theoretical studies have included the effects of the Zeeman, dipolar and exchange energies as well as those arising from the boundary conditions applicable to both thick and thin ferromagnetic films with surfaces bounded by either free space or conducting planes. Experimental studies involving single crystal YIG substrates have already commenced.

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V. CRYSTAL PHYSICS AND OPTICAL ELECTRONICS LABORATORY

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* Dr. D. Gabbe, DSR Staff
* E. Farrell, DSR Staff
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* A. Vetrovs, Technical Assistant
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* Mrs. Delphine Radcliffe, Secretary

Personnel who have left

  O. Braaten - returned to Norway
  C. A. Clark - graduated from Northeastern University
  Mrs. A. Szorc, DSR Staff - returned to school.

Degrees Granted

O. Braaten, S.B., Electrical Engineering, June 1970.

L. T. Todd, S.M., Electrical Engineering, June 1970.

Sponsorship

Advanced Research Projects Agency, SD90, DSR-75111, 78894, 71623
(all above terminated on June 30, 1970).

Advanced Research Projects Agency, DAHC 15 67 C 0222, DSR-72211, 72264, 72219

Advanced Research Projects Agency, DAHC 15 70 C 0190, DSR-72144.

NASA, ERC, Grant NGL 22-009-418, DSR-71647.

Office of Naval Research, Nonr-3963(20), DSR-74638 (terminated May 31, 1970).

Office of Naval Research, N00014-67-A-0204-0044, DSR-72339.

Office of Naval Research, N00014-67-A-0025, DSR-71101
(terminated November 30, 1969).

U.S. Air Force, WPAFB, Avionics Laboratory, F33615-68-C-1490, DSR-70963
(terminated March 15, 1970).

U.S. Army, MERDC, Night Vision Laboratory, DAAK02-69-C-0047, DSR-71308.

Research Report

1.0 Crystal Growth

1.1 Ferroelectric Crystals

Personnel: A. Linz; R. C. Folweiler; V. Belruss; E. F. Farrell; A. Vetrovs.

Sponsorship: Advanced Research Projects Agency
NASA/ERC
Air Force Avionics Laboratory

Top-seeded solution growth of ferroelectric crystals has continued where the crystals are required. This has included pure and doped $BaTiO_3$ for conductivity studies and $(K,Na)TaO_3$ and $K(Nb,Ta)O_3$ for Raman scattering and dielectric studies. Work is in progress on the growth of $(Ba,Sr)TiO_3$ crystals for Raman scattering and pyroelectric detector evaluation.

Lack of success in growing strain-free crystals of $Bi_4Ti_3O_{12}$ by the top-seeded solution technique indicated that another isothermal method must be found. The high vapor pressure of the appropriate chlorides suggested the possibility of chemical vapor deposition (CVD) process for the growth of appropriately oriented crystals. Work was initiated on TiO_2, since it is one component of the compound.

A CVD system capable of growing oxide crystals by reacting metal

chlorides with oxygen at elevated temperatures (1000 - 13000°C) under controlled pressures (ambient to less than one torr) has been assembled, including a gas distribution system (flow meters, switches, etc.), two feed reactors, a resistance wound tube furnace, a pressure detector and controls and a vacuum pump. Chlorine gas regulated from 17 psia is passed over the metal in the reactor where the metal chloride is formed, and pumped into the furnace with hydrogen and oxygen where the reaction occurs as: $TiCl_4 + 2\ H_2 + O_2 \rightleftarrows TiO_2 + 4\ HCl$. Excess chlorine is used to control the reaction. The oxide can crystallize on the walls of the furnace which is lined with a quartz tube, or alternatively crystallization may take place on a cooled seed rod while noncrystalline reactants, H_2O, HCl and Cl_2 pump out of the furnace into liquid nitrogen cooled traps. The reaction takes place under controlled pressure varied by bleeding nitrogen gas into the mechanical pump at a rate regulated by a pressure sensor and servo loop. Formation of small TiO_2 crystals has been obtained.

1.2 Germanates

Personnel: A. Linz; J. Kalnajs; V. Belruss

Sponsorship: Army Night Vision Laboratory
Office of Naval Research

Work on growth of complex rare earth germanate garnets is continuing. These materials show great promise as medium gain laser host crystals. Various substituted garnet systems such as $Ba_{0.25}Mg_{0.75}Y_2Mg_2Ge_3O_{12}$ (BAMGAR) and others are being explored, along with possible new compounds.

1.3 High Temperature Oxides

Personnel: A. Linz; E. F. Farrell; A. Vetrovs.

Sponsorship: Advanced Research Projects Agency
Air Force Avionics Laboratory

R.F. Czochralski growth of $Gd_2(MoO_4)_3$ and $(Gd,Y)_2(MoO_4)_3$ crystals for ferroelectric research is continuing as needed. Flame fusion growth of transition metal oxides is being abandoned in favor of vapor phase techniques which yield much higher quality crystals.

1.4 Fluorides

Personnel: A. Linz; D. Gabbe; R. Mills.

Sponsorship: Advanced Research Projects Agency
Office of Naval Research

1.4.1 Zone Refining

A high vacuum/inert gas zone-refiner heated by RF means has now been

built. The unit is a water-cooled stainless steel cylinder fitted with the appropriate access doors and power feed-throughs. Mechanical motion of the charge is activated by an external screw mechanism which drives a parallel pair of water-cooled support bars through vacuum seals in the chamber walls. The charge will be contained in a vitreous carbon boat. A hemicylindrical graphite piece serves as both boat support and susceptor. The chief goal of zone refining is to produce rigorously oxygen-free fluorides for use as starting materials for the growth of single crystals.

1.4.2 Crystal Growth Furnaces

In cooperation with the Norton Company, one of the laboratory's fluoride crystal-pulling furnaces has been converted to a dual chamber unit which functions as an interlock between the work chamber and the atmosphere. This feature allows much better cleanup of the melt surface than could be achieved with the single chamber furnace. The charge is not re-exposed to the atmosphere at any time during the crystal growth process. Thus the recontamination that was incurred previously when the furnace had to be opened for removal of collected surface contamination is obviated by use of the interlock feature. With a well-cleaned melt surface available for the first time, crystal growth and especially seeding are no longer disturbed by the presence of foreign particles which initiate the formation of low-angle grain boundaries. The other of our two fluoride crystal-pullers is being modified similarly in our shop.

1.4.3 Lithium Yttrium Fluoride

Many $LiYF_4$ crystals doped with rare earths, singly and in various combinations have been grown for spectroscopic and laser studies.

1.4.4 Yttrium Fluoride - Ytterbium Fluoride

Yttrium fluoride-ytterbium fluoride mixed crystals doped with various rare earths are being grown for infrared to visible conversion devices. A phase transition in the region of 1000°C requires that crystal growth be carried out from a suitable solution. At a melt composition of about 40 mol % LiF, the low temperature phase becomes the primary one.

1.4.5 Potassium Manganese Fluoride

Crystals of $KMnF_3$ were grown for neutron scattering. Experiments at Brookhaven National Laboratories indicated a very low mosaic spread (< 1').

1.5 Synthesis and Purification of Materials

Personnel: D. Gabbe, C. A. Clark.

Sponsorship: Advanced Research Projects Agency
Office of Naval Research

1.5.1 Zone Refining

Two resistance heated zone refiners capable of operation up to 1000°C have been placed in operation. Both are three-zone units with the temperature of each zone independently regulated by an on/off controller. The charge is contained in a vitreous carbon boat measuring 1.7 inches in diameter and 18 inches long. The boat and charge are protected from the atmosphere by a quartz tube, sealed at one end, capped at the other with a vacuum-tight cap. A valve in the cap permits connection to a vacuum system. Vitreous carbon is a distinct improvement over the quartz containers used previously which frequently cracked as a result of attack by oxides in the charge. These zone-refiners are used for the purification of starting materials used in the preparation of feed for the growth of various single crystals.

1.5.2 Barium Titanate

Experimental studies of conduction processes in barium titanate require that crystals be grown that are at least an order of magnitude purer than those presently available. We have therefore undertaken the preparation of highly purified barium titanate feed (starting material for crystal growth) under conditions of strict cleanliness. The starting materials are barium chloride, titanium tetrachloride and oxalic acid. Barium chloride is purified by a solvent extraction process designed to remove aluminum and transition metals followed by zone refining to remove alkali metals and silica. Neat titanium tetrachloride is purified by recrystallization in the normal freezing mode. Special glassware has been designed to minimize recontamination of the purified $TiCl_4$. Oxalic acid is purified by a solvent extraction process. To avoid recontamination of the purified materials, chemical apparatus normally made of metal, such as supports, clamps, etc., has been made from plastic.

1.5.3 Titanium Dioxide

Purified TiO_2 is also required for the growth of barium titanate crystals, and is prepared in analagous fashion to barium titanate feed.

1.5.4 Rubidium Manganese Fluoride

The synthesis of ultra-pure $RbMnF_3$ crystals is being carried out with a view toward characterizing the relationship between impurities and the magnetic properties of $RbMnF_3$. Rubidium chloride with a purity at least two orders of magnitude better than the material which was previously used is now available. An ion exchange process was developed for converting RbCl to the Rb_2CO_3 necessary for the synthesis of $RbMnF_3$. Purification of the manganese was done by zone refining reagent grade $MnCl_2$.

2.0 Crystal and Electro-optical Research

2.1 Ferroelectric Studies

2.1.1 Dielectric and Optical Studies

Personnel: T. G. Davis; L. T. Todd.

Sponsorship: Advanced Research Projects Agency
Air Force Avionics Laboratory

In the ferroelectric mixed-crystal system $K(Ta_x,Nb_{1-x})O_3$, crystals containing small amounts of niobium undergo ferroelectric transitions which are thermodynamically second-order. With increasing niobium concentration, the transitions become first-order. By means of Raman spectroscopy, we have observed "soft" ferroelectric phonons associated with the phase transitions in all compositions. In those compositions which are first-order, the soft mode appears to be heavily overdamped. Second-order transitions seem to be associated with well-defined underdamped soft modes.

In the course of the investigation, a novel technique was developed for measuring polarization dependence of the small-signal dielectric constant in materials having high loss factor. Using this technique, we have measured temperature dependence of the P^4 term in the Devonshire free energy expansion for a wide range of compositions, and consequently obtained an accurate value of the critical composition which divides first- and second-order regions.

The observed correlation of damping of the soft mode and thermodynamic order of the transition has suggested several additional experiments. In the coming year, we intend to pursue studies of mixed-crystal ferroelectrics such as $(Ba,Sr)TiO_3$, and to initiate a study of pressure dependence of the soft mode frequency in single-component perovskites which undergo transitions at convenient temperatures, particularly barium titanate.

2.1.2 Optical Ferroelectrics

Personnel: D. J. Epstein; W. V. Herrick.

Sponsorship: Advanced Research Projects Agency; A.F. Avionics Laboratory.

Gadolinium molybdate, $Gd_2(MoO_4)_3$, is an unusual ferroelectric in that the temperature dependence of the dielectric permittivity in no way resembles the Curie-Weiss behavior of the typical ferroelectric. Between room temperature and 200°C the clamped dielectric constant, measured along the polar c-axis, has essentially a constant value ($\kappa \simeq 10$) and shows no discontinuity whatsoever at the Curie point (159°C). The free dielectric constant shows a slight anomaly but only as a consequence of a change in the piezoelectric properties.

In the usual ferroelectric, the phase transformation is identified with the instability of a transverse optical mode, and, indeed, it is the tempera-

ture induced "softening" of this mode that results in the Curie-Weiss behavior characteristic of the paraelectric region. It has been suggested that in gadolinium molybdate the ferroelectric state is to be identified with an unstable acoustic mode, the instability resulting in a spontaneous strain which via piezoelectric coupling produces the spontaneous polarization.

To obtain some insight into questions of mode instabilities we have measured the temperature dependence of a number of the elastic constants of $Gd_2(MoO_4)_3$ over the range 20 - 200°C using a pulse-echo technique at 10 MHz. The paraelectric phase is characterized by 6 independent elastic constants; of these we have this far measured the four diagonal constants C_{11}, C_{33}, C_{44} and C_{66}. In passing through the para-to-ferroelectric transformation at 160°C, C_{11} shows an extremely pronounced "softening;" the other constants undergo no significant change.

2.1.3 Semiconducting Ferroelectrics

Personnel: D. J. Epstein; J. S. Fuhrer.

Sponsorship: NASA/ERC

Advanced Research Projects Agency

The properties and possible device applications of semiconducting barium titanate crystals are being investigated by Mr. J. S. Fuhrer. Pure barium titanate is a ferroelectric material with a room temperature resistivity in excess of 10^9 ohm cm. However, the addition of such dopants as La, Nb, Gd, Ce and W converts the material to an n-type, low mobility semiconductor. We have been able to grow, by the top-seeded solution technique, a variety of large single crystals, doped as above, which have resistivities in the range 1 - 100 ohm cm. However, when we attempt to grow crystals of somewhat higher resistivity, by lowering the dopant concentration, we obtain insulating crystals. Our present belief is that low dopant concentrations are being compensated by trace impurities. To overcome this difficulty we have undertaken a program to produce high purity barium titanate feed.

The conductivity anisotropy in the tetragonal phase of Nb doped barium titanate has been measured in several single domain samples and the results are found to agree with those previously reported for reduced barium titanate. None of our crystals show the PTC effect that has been found in doped ceramics, a result which supports the argument that PTC behavior is a grain boundary phenomenon.

Schottky diodes fabricated on several semiconducting ferroelectric crystals have been found to show an I-V characteristic that depends on the polarization state of the ferroelectric. This behavior, if it can be adequately controlled, has possibilities for data storage applications.

2.2 Optically Pumped Laser Crystal Research

2.2.1 Sensitized Luminescence in Rare Earth Fluorides

Personnel: A. Linz; H. P. Jenssen.

Sponsorship: Advanced Research Projects Agency
Office of Naval Research

Energy transfer between rare earth ions in $LiYF_4$ is under study. The purpose of the study is to investigate the role of phonon participation in the transfer process. In most cases phonons are necessary to make up for the energy mismatch between the initial and final electronic states of the system. The theory for energy transfer as developed by Dexter predicted that the transfer probability should be proportional to the overlap integral of energy of the initial and final states. But transfer does take place when there is no overlap even when the vibronic sidebands are included. It is known that an excited ion can relax to its next lower level by a multi-phonon process. This process is faster than radiative decay even when 4 to 5 phonons are involved. A multiphonon relaxation seems to be the only explanation for the nonresonant transfer process.

The orbit-lattice interaction can best be observed as vibronic sidebands in absorption and fluorescence. This has been done for several rare earth ions in $LiYF_4$. The vibronic structure varies little for different ions and different transitions in each ion. Most of the sharp vibronic lines are in agreement with published phonon energies in $LiYF_4$ determined by Raman scattering and infrared absorption. The strength of the vibronics varies from being almost undetectable to a strength of about the same order of magnitude as the parent transition. Preliminary studies on transfer seem to indicate that levels with strong vibronics are more efficient as sensitizers, but this will be studied further. Multiphonon relaxation will also be studied to see if the strength of the vibronics affects the relaxation rate.

Energy transfer has been observed in $LiYF_4$ with Yb^{3+} as sensitizer and Er^{3+} as activator. Here two successive transfers lead to upconversion of light, but the process does not seem to be as efficient as published for other hosts.

Crystals with Er^{3+} and Ho^{3+} are under study. Transfer here seems to take place between several levels in both ions and in both directions. It is the intention to measure the transfer rates as a function of the energy mismatch. Vibronic intensities, multiphonon decay rates and fluorescent lifetimes of all levels involved will be measured in crystals with only one of the rare earth ions present. Crystals with other pairs of rare earth ions will also be investigated and different host crystals will also be used.

2.2.2 Optically Pumped Visible Lasers

Personnel: A. Linz; E. K. Chan.

Sponsorship: Office of Naval Research

Stimulated emission has been achieved in different host crystals doped with various rare earth ions, among which only a few were reported to lase in the visible region. The rest fall in the infrared. In part this can be attributed to the high threshold conditions at shorter wavelengths due to the proximity of other rare earth ion levels, and the difficulty of obtaining adequate pumping band strengths. However, most of the work with rare earth ions emitting in the visible was done either with hosts such as CaF_2 or $CaWO_4$ where charge compensation had deleterious effects or with materials such as LaF_3 where only poor quality crystals were available. YLF offers an opportunity for testing these ions in a high optical quality fluoride host where no charge compensation mechanism is necessary.

Preliminary work with Ho^{3+} and Er^{3+} in $LiYF_4$ has indicated that Er^{3+} by itself is the best candidate found so far. A strong fluorescence line at 5510 Å has a lifetime of 270 microseconds at room temperature and 690 microseconds at 77°K in a 2 mol % doping concentration. A small rod has been fabricated and is currently being tested in an exfocal coolable ellipsoidal cavity. This study is being continued with other dopings and larger and higher perfection rods to see if we can obtain a reasonably efficient green laser. Sensitizers such as Gd^{3+} in large amounts in the host crystal, i.e., $LiGdF_4$, will also be tried. As results are obtained from energy transfer measurements with other ions in other lattices, these results will be used in the laser development program with large enough crystals for laser testing.

2.2.3 Fluorescence of Nd^{3+} in Complex Germanate Garnets

Personnel: A. Linz; J. Kalnajs; E. K. Chan.

Sponsorship: Advanced Research Projects Agency
Army Night Vision Laboratory

There is a general need for laser materials having a gain somewhere between glasses and high gain crystals such as yttrium aluminum garnet (YAG) Particularly for 1.06 μm Nd^{3+} lasers, these materials are needed for Q-spoiled operation where large energy storage combined with a high damage threshold is required. Materials with more output at 9400 Å are also desired. Germanate garnets were investigated with particular attention paid to analogs in known silicate systems. In nature many substances are possible with garnet structures and a few rare earth garnets are known. In particular, a calcium yttrium zinc germanate garnet was grown but this material changed composition during growth and as a result was highly strained and yielded cracked crystals.

It did have the interesting property that the branching ratio for an incorporated Nd^{3+} ion was very different from YAG and in particular much more energy went into the 9400 Å transition to the ground state in comparison to the 1.06 μm laser transition. However, laser quality crystals of this material could not be grown.

In an effort to find another garnet which would have better growth properties, an attempt was made to grow a crystal from a barium yttrium magnesium germanate melt. This material grows quite well and crystals up to 4 cm diameter were obtained without cracking or strain. However, lattice constant and density determination show that they are not the ideal $BaY_2Mg_2Ge_3O_{12}$ composition, but in fact must contain somewhat less of the heavier ions. The nominal composition appears to be $(Ba_{0.25}Mg_{0.75})Y_2Mg_2Ge_3O_{12}$ with some of the magnesium apparently substituting for the barium. The branching ratio of the Nd^{3+} ion substituted in this material appears to be comparable to that found in YAG and Nd^{3+} glasses. Crystals of this material, nicknamed BAMGAR, show very desirable intermediate gain properties when doped with Nd^{3+}. Linewidths are of the order of 50 Å, and lifetimes are of the order of 300 microseconds for the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition. Particularly in the case of BAMGAR, these crystals are of very high optical quality, show no scattering and appear to be exactly what is desired for high peak power Q-spoiled operation.

The variability in composition of these materials allows one to tailor the linewidths, lifetimes and crystal field splitting for the application desired. Preliminary experimental work with $CaY_2(Zn,Mg)_2Ge_3O_{12}$ shows promise of combining good crystal quality with high output at 9400 Å.

2.2.4 Physical Properties of Laser Host Crystals

Personnel: J. Kalnajs

Sponsorship: Advanced Research Projects Agency
Office of Naval Research

Thermal conductivity is one of the most important physical properties in a laser host material, since it plays a large role in damage threshold and lensing effects. Equipment for measuring this physical quantity based on the steady state heat flow principle was assembled. At present with our set-up the thermal conductivity of crystals can be determined at ambient temperature but expansion of the measurements to higher and lower temperatures is planned. Performance of the equipment has been checked, using fused quartz and oriented rutile samples; the results compare well with the published data.

The thermal conductivity of tetragonal $LiYF_4$:Nd was found to be 77×10^{-4} along [001] and 94×10^{-4} along [110] in cal cm/sec cm^2 °C. For

the $BaY_2Mg_2Ge_3O_{12}$ garnet, a value of 66 x 10^{-4} was found. These compare to about 300 x 10^{-4} for YAG and 10 - 20 x 10^{-4} for most glasses.

2.3 Dielectric Spectroscopy

Personnel: A. Smakula; A. Szorc.

Sponsorship: Advanced Research Projects Agency

In continuation of our research of dielectric properties of semiconductors at low temperatures the following topics were studied: The influence of frequency of the applied electric field on the dielectric constant κ' and the dielectric loss κ''; the influence of dopant concentration; the influence of dopants.

The sharp change of κ' as a function of temperature shifts in all cases (n-type, p-type and compensated Si) toward higher temperature as the frequency increases. κ'' always reaches a maximum value at a temperature where the κ' shows the inflection point. On changing the frequency from 10^3 to 10^6 Hz, the κ''_{max} shifts by 13°K. The temperature halfwidth of κ'' is 2°K for Si doped with B or with P, and 3.5°K for Si doped with P + B. The temperature of κ''_{max} increases with conductivity in the n-type and decreases in the p-type. The height of the κ' plateau and the maximum of κ'' increase with the concentration of charge carriers. Additional sharp changes of κ' and maxima of κ'' have been discovered in a p-type Si sample of very high resistivity (30,000 ohm cm). These discontinuities of κ' and κ'' can belong either to various impurities (dopants) or to higher excited states of one impurity. The possibility of higher excited states is more probable.

Silicon doped with antimony ($n = 5 \times 10^{16}/cm^3$) shows a very similar variation of κ' and κ'' with temperature to Si doped with P. The only difference is a shift of κ''_{max} toward lower temperature.

Preliminary results obtained on Si doped with As indicate that the position of κ''_{max} lies at somewhat higher temperatures than that of Si doped with P and Sb.

The observed dielectric effects are explained by thermal excitation of dopants (impurities). The energies are of the order of 10^{-3} eV, similar to optical excitation. It is intended to apply this method to other crystals and dopants.

2.4 Investigation of CdS, In_2S_3 and $CdS \cdot In_2S_3$ Crystals

Personnel: A. Smakula; J. Kalnajs.

Sponsorship: Office of Naval Research.

Two properties are decisive in high power CO_2 laser windows: high mechanical strength and low optical absorption. Some semiconducting

crystals have high strength but do not show low enough absorption at 10.6 μm. The relatively high absorption can be caused by free charge carriers, impurities, or multiphonon absorption. In some cases the free charge carriers can be suppressed, e.g., by doping GaSb with Li, but introducing foreign atoms into a lattice may cause additional absorption. It was of interest to study a system where two different cations can be studied separately and together and see whether the absorption will be increased. We selected for this purpose two binary compounds, CdS and In_2S_3, and the ternary compound $CdS \cdot In_2S_3$.

CdS grown from vapor phase is generally n-type, having an excess of Cd ions. Such crystals show low resistivity and poor transmission in the infrared. Crystals grown from material with an excess of S have resistivity higher than 10^6 ohm cm and no detectable absorption from 0.52 to 14 μm. The absorption edge at short wavelength 0.52 μm corresponds to indirect band-to-band electronic transitions. At wavelengths longer than 14 μm the absorption increases continuously. Our sample had a resistivity of 10^6 ohm cm, high energy absorption edge at 0.52 μm and low energy at 14 μm. A sharp absorption band has been observed at 16.9 μm. The optical transverse mode wavelength is at 42.7 and 41.5 μm. No increase of absorption toward longer wavelengths has been observed in the transmission region from 0.52 to 14 μm. This indicates that free charge carriers are not present.

In_2S_3 was purified by H_2S at 250°C. Crystals were grown by chemical transport reaction using iodine for intermediate reaction and volatilization. The reaction temperature was 800°C and deposition temperature 600°C. Dark red crystals up to 5 mm in size were obtained in 48 hours. The short wavelength absorption edge of In_2S_3 crystals is at 0.675 μm and on the long wavelength side at 12 μm. Similar to CdS, the In_2S_3 has a sharp absorption band at 14.5 μm.

The $CdS \cdot In_2S_3$ crystals were grown from stoichiometric composition of CdS and In_2S_3 by chemical transport method similar to that for pure In_2S_3. The largest crystals were only 8 mm in size. Variation of growing conditions (changing the shape of the reaction tube, adding S or Te, changing the I_2 concentration, variation of temperature of reaction and deposition) did not lead to larger crystals. The main obstacle is the excessive nucleation.

The absorption edge of $CdS \cdot In_2S_3$ in the visible is at 0.575 and in infrared at 14 μm. Three absorption peaks at 15, 15.6 and 17 μm appear. Similar to both binary systems, CdS and In_2S_3, the ternary system $CdS \cdot In_2S_4$ does not show any additional absorption in the transmission range.

All three crystals show relatively high absorption using a high

intensity laser beam at 10.6 μm, a hundred times higher than in useful ionic crystals. Since there is no noticeable absorption by free charge carriers we have to assume that the high absorption is caused by multi-phonon processes. This assumption is in agreement with the close proximity of the infrared absorption edges, but further study is required for confirmation.

2.5 Cathodochromic Materials

Personnel: A. Linz; E. F. Farrell; A. Verrovs.

Sponsorship: Advanced Research Projects Agency.

The cubic mineral sodalite $Na_8Cl_2[AlSiO_4]_6$ is a photochromic and cathodochromatic material which can be either optically or thermally bleached, depending on composition. These properties make sodalite a promising material for use in cathode ray tube displays where a storable image viewable under high ambient light conditions is desired. Crystals of sodalite are being grown by hydrothermal techniques. The effects of substitutions for various ions in the lattice and of different post growth heat treatment will be studied. A demountable cathode ray tube system for testing is being designed. Techniques for the preparation of powders are also under study.

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I PHYSICS OF SOLIDS

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Degrees Granted:

R. Currat, Ph.D., August 1969, Metallurgy and Materials Science

M. Kuninsky, M.S., June 1970, Physics

S. Lee, M.S., August 1969, Metallurgy and Materials Science

J. Linderman, M.S., June 1970, Electrical Engineering

K. R. Morash, Ph.D., August 1969, Metallurgy and Materials Science

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Sponsorship:

* Advanced Research Projects Agency, SD-90, DSR 71622, 71626, 72282, 72521, 75121, 75123, 75125, 78882, 78883, 78892, 78897; GP-21312, 72654; DAHC15-67-C-0222, 72221, 72223, 72232, 72273, 72293

Air Force Office of Scientific Research, F44620-69-C-0054, DSR 71446

Army Research Office, DAHC04-70-C-0045, DSR 72521

National Aeronautics and Space Administration, NAS12-2040, DSR 71329

National Science Foundation, GK-1947, DSR 70847; GJ-129, DSR 71743; GP-21312, DSR 72654

Office of Naval Research, N00014-67-A-0204-0027, DSR 71362

Wright Air Development Center, F33615-67-C-1126, DSR 70321

Xerox Research Corporation, DSR 74997

Research Report

Research in the Physics of Solids group is centered about applications of quantum mechanics to the behavior of electrons in materials. Particular emphasis is based in evaluating the role of structure in these properties. The general areas of research include: the structure of amorphous materials, behaviour of amorphous semiconductors, photoconductivity, spin correlations and critical phenomena in magnetic materials, magnetism in alloys, Fermi surfaces, and band calculations in alloys and compounds.

1.0 Spin Correlations and Critical Phenomena in Magnetic Materials

Personnel: B. L. Averbach; K. R. Morash and M. D. Rechtin

Sponsorship: National Science Foundation

Magnetic neutron scattering measurements have been made on a single crystal of CoO. The antiferromagnetic ordering below the critical temperature (T_N = 16°C) is such that spins are parallel on a given {111} plane, with adjacent planes in an antiparallel arrangement. We have shown that the spins are tipped at an angle of 7°50' out of the {111} planes, and we have followed the development of long range order down to 4.2°K. The long range order appears to follow a Heisenberg spin wave model for temperatures between 4.2°K and $0.97T_N$. From $0.97T_N$ to T_N the long range order seems to decay in an Ising manner. The (111) diffuse magnetic neutron intensity, due to regions of dynamic short range spin correlation, was also measured near T_N.

Within the critical region, $|(T-T_N)/T_N| \lesssim .04$, the long range magnetic order decay was characterized by the critical exponent $\beta = 0.244 \pm .015$. This exponent is referred to a lattice in which there is a large tetragonal contraction associated with the spontaneous magnetization. Upon correcting to a rigid lattice state, there was an apparent increase of T_N with tetragonal deformation, and the corrected critical exponent $\beta = 0.29 \pm .025$ is in agreement with the predicted Ising behavior in the critical region. Since the long range order outside the critical region follows a spin wave behavior there is evidently

a change from a Heisenberg to Ising interaction near the critical area.

A density increase was measured by dilatometer on passing through T_N. This density change in the critical region, related to the spontaneous magnetization, was also described by the exponent β and resulted in a value $\beta = 0.36 \pm .05$. This was corrected to a rigid lattice and agreed within the experimental accuracy of the neutron scattering value.

The diffuse neutron intensity near the (111) point was measured at temperatures above and below T_N within the critical region. We determined that the exponents γ and γ', which describe the decay of diffuse intensity at the (111) point above and below T_N, respectively, were equal within 5%. Applying scaling law relationships between α (specific heat exponent), β, and γ, we found $\gamma = 1.30 \pm .06$, which is close to the accepted Ising prediction of 1.25.

The localized magnetic structure above T_N was determined at $T/T_N = 1.03$ and 1.07 by measurements of the (111) magnetic diffuse peak in the $(h_1 h_1 h_3)$ plane of reciprocal space. Applying the Cowley treatment to these data, we obtained spin correlations out to fifty neighbors. The first ten short range order parameters are:

T/T_N	α_0	α_1	α_2	α_3	α_4	α_5	α_6	α_7	α_8	α_9
1.03	1.0	-.035	-.360	+.015	+.220	+.007	-.155	+.005	+.125	+.004
1.07	1.0	-.030	-.310	+.013	+.175	+.006	-.125	+.004	+.093	+.003

where α_i is the spin correlation function $\langle \vec{S}_o \cdot \vec{S}_i \rangle / S(S+1)$, or in terms of probabilities $\alpha_i = 1-2P_i$ where P_i is the probability of finding an up spin as the i-th neighbor of a down spin. The short range order parameters for unmixed shells (i = even) indicated the maintenance of the basic characteristics of the layered spin arrangement on a local basis even at temperatures above T_N, and the correlation appeared to follow an Ornstein-Zernike decay. The inverse correlation range parameters were $K_1 = (13.3A)^{-1}$ and $(11.3A)^{-1}$ for $T/T_N = 1.03$ and 1.07, respectively. Strain measurements above T_N along the [001] direction revealed a small tetragonal deformation, which persisted at least to $T/T_N = 1.10$, indicating that tetragonal

and spin domains remained above T_N. The nearest neighbor spin correlations were not zero, as they are at temperatures below T_N, but antiparallel, like the second neighbors. Using the Cowley analysis, this yielded positive interaction potentials, V_1 and V_2, of 58k and 113k for $T/T_N = 1.03$ and 31.8k and 110k at $T/T_N = 1.07$. An order-disorder treatment of Moss and Clapp also showed V_1 to be comparable in magnitude to V_2. These data indicate that both the nearest and next nearest neighbor interactions are important in the magnetic structure of CoO above T_N.

2.0 Atomic Arrangements in Selenium-Arsenic Alloys

Personnel: B. L. Averbach; A. Renninger
Sponsorship: Xerox Corporation

The structure of amorphous and crystalline alloys of selenium-arsenic are being determined. The alloys As_2Se_3 and As_4Se_4 are now being investigated. X-ray diffraction data are being used to obtain radial distribution functions and these are then interpreted by means of computer models. Preliminary results indicate that the structure of amorphous As_2Se_3 is closely related to that of the crystalline compound. It appears that the molecular structure is retained in the amorphous material. However, there are a sufficient number of local perturbations to destroy the long range crystalline correlation.

3.0 Photoconductivity in Amorphous Materials

Personnel: B. L. Averbach; K. R. Morash, J. A. Woollam, M. Kuninsky
Sponsorship: Advanced Research Projects Agency

Measurements are being made of the photoconductivity in selenium as a function of temperature. Measurements of the drift mobility in films of vitreous selenium varying in thickness from 20 microns to 50 microns have been made as a function of temperature in the range $191^{\circ}K$ to $295^{\circ}K$. Electric fields applied to the samples varied up to 9×10^4 V/cm. A value of about 5.5×10^{-3} cm^2/V-sec was obtained for the electron drift mobility at room temperature. The hole drift mobility varied from .135 cm^2/V-sec at room temperature to .021

at 228°K to .00293 at 191°K. The activation energy obtained from the temperature dependence of u_h is .919 eV.

Measurements of hole drift mobility made on samples deposited above and below the glass transition temperature show few variations between the two types. The room temperature trapping time of 30 usec was found to increase by at least an order of magnitude as the temperature was lowered to 191°K.

An attempt to measure the magnetoresistance in these samples showed that $\Delta\rho/\rho$ is smaller than 0.05.

4.0 The Structure of Amorphous Semiconductors

Personnel: B. L. Averbach; M. Rechtin, H. Beumer
Sponsorship: Advanced Research Projects Agency

The structure of several amorphous semiconductors are being determined by means of X-ray diffraction. The principal semiconductors to be investigated are of the Te-Ge-As, Se-As and Te-Ge-As-Si types. Memory and switching types of semiconductors are being studied. An attempt will be made to determine the changes in structure which occur on switching.

5.0 Magnetic Materials

Personnel: B. L. Averbach; H. Beumer
Sponsorship: National Science Foundation

The structure of rare earth-cobalt magnetic compounds is being investigated. The magnetic susceptibility of fine particles produced by splat cooling is being compared with magnetically processed powders. The distribution of moments is also being studied by means of magnetic neutron scattering.

6.0 The Structure of Liquids

Personnel: R. Kaplow, B. L. Averbach; S. C. Lee
Sponsorship: National Science Foundation

The radial distribution of atom pairs in water and in solutions of hydrochloric acid have been measured by X-ray diffraction. The near-neighbor water correlations are strongly affected by the ions. Part of the experimental distribution is attributed to new oxygen-to-oxygen distances, associated with

the presence of excess protons, and these distances become shorter as the concentration of the acid increases.

Statistical thermodynamic and dynamical calculations are feasible which relate the pair distribution functions of liquids to presumed interaction potentials between the atoms. Ordinarily, the assumption is made that such interactions are spherically symmetrical (that is radial pair potentials are used). This simplification may not be reasonable, particularly in systems of low local symmetry. We are therefore programming numerical iteration solutions to the many body equations of motion, allowing angular (three-body dependent) terms as well as radial terms in the potentials. These will be used to study dynamic effects and equilibrium distributions in dense liquids with strong local asymmetries.

7.0 Compton Scattering

Personnel: R. Kaplow (Peter DeCicco); R. Currat

Sponsorship: Wright Air Development Center (and Advanced Research Projects Agency)

Compton scattered X-ray spectra were measured for three orientations of a beryllium single crystal. The reduced profiles were analyzed in terms of the electron momentum distribution. Observed anisotropies can be explained qualitatively in terms of the geometry of the Fermi surface and are in qualitative agreement with earlier positron and X-ray data. The present results show high momentum components among the valence electrons which are not revealed in the positron experiment nor accounted for by available calculations. In the process of reducing the data to obtain the momentum distribution of the valence electrons, detailed consideration was given to the effects of binding upon the Compton scattering by the core electrons.

8.0 Mossbauer Effect in Iron Alloys

Personnel: R. Kaplow; W. K. Choo (in cooperation with Professor M. Cohen)

Sponsorship: Office of Naval Research

High resolution Mossbauer data are being obtained for

splat-cooled high carbon specimens. Measurements have been made of the martensitic phase formed during cooling to liquid nitrogen temperature, at this temperature to minimize thermal aging. Such spectra are like those previously observed in martensite formed at higher temperatures and indicate that certain features are independent of aging effects which may have occurred. Careful studies are underway to correlate changes in the Mossbauer spectra with strength and electrical resistivity variations during aging at and below room temperature. Theoretical calculations are also being attempted to relate the spectral features to alterations in the iron atom electron spin polarization (hyperfine field effect) caused by particular carbon atom configurations.

In a separate study, cold worked (abrasive filed) iron powders show no detectable broadening in the Mossbauer spectra, in spite of deformations which yield significant broadening of X-ray diffraction lines.

9.0 The Structure of SiO

Personnel: R. Kaplow; J. Yasaitis

Sponsorship: Advanced Research Projects Agency

The radial distribution function of amorphous SiO has been measured using both copper and molybdenum characteristic radiation. Contrary to earlier results, we find that SiO is not describable as a mixture of amorphous SiO_2 and Si. Although a unique structure has not been determined, the data appears consistent with a model of connected rings, perhaps puckered, as is suggested by the form of the gaseous molecule and by studies of condensation in rare gas matrices.

10.0 Teacher-Interactive Computer System

Personnel: R. Kaplow; F. C. Smith, A. Campagna; J. Linderman; D. Schneider, W. Stensrud, L. Scheffler, S. Cohen, R. Baron

Sponsorship: National Science Foundation

An on-line computer sub-system has been designed and is being implemented, with the purpose of providing an effective mechanism for teachers to develop computerized tutorial programs.

Programs have been written for all major aspects of the system; including the operators for the creation and editing of the teacher's active description of the tutorial, as well as for simulation. Debugging and testing of the operation of the system as a whole is underway. The system includes extensive keyword indexing features and a separable dictionary-thesaurus facility.

11.0 Alloy Photo-Emission and Surface Effects

Personnel: R. Kaplow; W. Ewing

Sponsorship: Advanced Research Projects Agency

A high-vacuum electron spectrometer has been assembled for the purpose of measuring the intensity and energy distribution of electrons emitted in response to ultraviolet excitation. Metal and alloy surfaces will be examined in various controlled conditions in order to study the distribution of electron states, and the nature and effects of surface conditions. Initial studies of methods for in situ cleaning of bulk specimen surfaces are in progress.

12.0 Experimental Study of Electrons in Complex Solids

Personnel: D. J. Sellmyer

Sponsorship: National Science Foundation

The object of this research is the study of the electronic states in solids of intermediate structural complexity. While we now have a quantitative understanding of elemental metals, semiconductors and simple ionic solids, our knowledge of solids such as disordered alloys, compounds with large numbers of atoms per primitive cell, and molecular-type solids is very primitive. In this work Fermi surface techniques such as the de Haas-van Alphen effect are being used to investigate metallic compounds with complex structures, electronic states associated with dilute impurities, and band structure effects in the screening of impurities.

13.0 Physics of Solids at High Magnetic Fields

Personnel: D. J. Sellmyer; J. Woollam, I. Goldstein

Sponsorship: National Science Foundation

In this work we are using strong magnetic fields to study several topics of high current interest. Transport and quantum oscillatory measurements are done in our 100 kG superconducting solenoid and in fields up to 220 kG at the Francis Bitter National Laboratory. The high fields are used either to study electronic or magnetic interactions by overriding them with the magnetic field or to get relatively dirty materials into the high field region ($\omega_c\tau > 1$). For example, preliminary analysis of recently obtained magnetoresistance data in pure beryllium indicates that the characteristic field for magnetic breakdown between the first and second bands is $\simeq$ 30 kG. In addition, experiments have been completed recently on quantum limit phenomena in pure graphite in fields up to 210 kG. Experiments planned for the near future are studies of the breakup of the spin-compensated state in the Kondo effect in noble metal alloys, and high-field magnetoresistance and Shubnikov-de Haas effect in pure cobalt.

14.0 Thermoelectricity in Magnetic Alloys

Personnel: D. J. Sellmyer; J. Zagarins

Sponsorship: National Aeronautics and Space Administration

An experimental investigation of the thermoelectric power and resistivity of magnetic impurity doped alloys is in progress. The object is the study of the spin-flip scattering process as it manifests itself in the thermopower. Two effects are being studied in particular: the effect of varying the host parameters such as the density of states, and the influence of potential scattering due to nonmagnetic impurities on the spin-flip scattering. An automatic data acquisition system has been installed for rapid measurements and computer analysis, and measurements are proceeding on AgPd(Fe) alloys.

15.0 Magnetic Moment Interactions in Dilute Magnetic Alloys

Personnel: D. J. Sellmyer; J. Franz

Sponsorship: Advanced Research Projects Agency

The object of this work is to study the interactions among localized magnetic moments in metals through the conduction

electrons. The concentrations of magnetic impurities are varied from the dilute (noninteracting) region to the region where some form of magnetic ordering occurs at low temperatures. The alloy systems being studied are copper and silver hosts with manganese and iron impurities. Low field susceptibility experiments are being performed between 4.2 and 300 K. These will be supplemented by magnetization measurements to 100 kG at temperatures down to approximately $1^{\circ}K$.

16.0 Localized Moments and Weak Ferromagnetism in Intermetallic Compounds

Personnel: D. J. Sellmyer; J. Franz, G. R. Caskey

Sponsorship: Advanced Research Projects Agency

The effects of local environments have been investigated in several transition metal compounds. Magnetic susceptibility and transport measurements between 1.3 and 300 K have been used to obtain information on the localized impurity states associated with deviations from exact stoichiometry. In the series of compounds T M, where T is Ni, Co, or Fe and M is Al or Ga, a wide variety of magnetic behavior occurs as a result of band structure effects and localized magnetic moments formed on T atoms on in sites in the lattice. For dilute concentrations of exces .o in CoAl, Kondo effect behavior is observed in the resistivity, susceptibility and magnetoresistance. Estimates of T_K and J are 8 ± 2K and -1.3 eV. In the FeAl, CoAl and CoGa systems the moments on excess T atoms order ferromagnetically at higher concentrations. In NiAl the excess Ni atoms do not form localized moments; the transport anomalies that are observed appear to be connected with moments on Ni rich clusters. A molecular field model incorporating local environment effects has been developed which explains qualitatively the concentration dependence of the saturation moment and Curie temperature in the CoAl and CoGa systems.

17.0 Electronic Structure and Cohesive Properties of Beryllium

Personnel: K. H. Johnson; D. Klingspon (in cooperation with Prof. P. D. DeCicco, Physics Dept.)

Sponsorship: Advanced Research Projects Agency

Beryllium is an important structural material because of its high elastic modulus and low density. However, the applications of this metal are limited because it is brittle. Our investigation is directed toward a determination of the theoretical electronic structure and cohesive properties of beryllium and the changes which occur upon alloying and oxide formation. It is hoped that this research will lead to a better understanding of the unusual properties of beryllium and beryllium alloys. Graduate student, D. Klingspon, is currently calculating the self-consistent-field band structure of beryllium as a function of: (1) the choice of statistical exchange potential, (2) the c/a ratio of the hcp crystal lattice, and (3) "nonspherical" components of the crystal potential and charge density. The band-structure calculations will be used as the starting point for a determination of the cohesive energy and for an interpretation of the unusual elastic properties of beryllium. We plan also to investigate the electronic structures of beryllium oxide and several beryllium alloys.

18.0 Electronic Structures of Intermetallic Compounds

Personnel: K. H. Johnson; H. S. Kim

Sponsorship: Advanced Research Projects Agency and National Science Foundation

In this research, emphasis is currently being placed on the determination of the theoretical electronic structures of ordered beta-phase alloys having the cesium-chloride type crystal structure. Band-structure calculations have been carried out on the compound β'AuZn, completing a systematic study of the IB-IIB beta-phase alloys which began with ordered beta brass β'CuZn. This work has led to an explanation of the Fermi surfaces and unusual optical properties of these alloys, as well as to an interpretation of their alloy-phase stability. A systematic investigation of the electronic structures of transition-metal aluminides is in progress, with band-structure calculations having been completed for the compound β'NiAl. A theoretical study of the compounds β'FeAl and β'CoAl is now being carried out by graduate student, H. S. Kim. This work will be used as a basis for interpreting

the very interesting optical and magnetic properties of these alloys.

19.0 Electronic Structures of Polyatomic and Macro-Molecules

Personnel: K. H. Johnson; F. C. Smith, Jr.

Sponsorship: Air Force Office of Scientific Research

A new approach, based on multiple-scattering theory and Green's function formalism, has been developed for calculating from first quantum-mechanical principles the electronic structures of polyatomic and macro-molecules. The computational simplicity of the method and its applicability to molecules of arbitrary stereochemical geometry are of particular advantage in treating complex molecules where more conventional methods of quantum chemistry are difficult to implement. Self-consistent-field calculations by this technique have recently been completed for methane (CH_4) and the molecular ions, ammonium (NH_4^+), sulfate (SO_4^{2-}), and perchlorate (ClO_4^-). The theoretical results for sulfate and perchlorate have been used to explain ESCA chemical-shift data and ESR data recently measured for these oxy-anions in crystals (e.g., K_2SO_4). Spin-polarized self-consistent-field calculations are now in progress on transition-metal complexes such as MnO_4^-, MnO_4^{2-}, NiF_6^{4-}, and $Fe(CN)_6^{4-}$, in order to develop a quantitative theory of their optical, paramagnetic, and diamagnetic properties. Applications to transition-metal coordination polymers and biological macro-molecules are also planned.

20.0 Theory of Localized Impurity States

Personnel: K. H. Johnson

Sponsorship: Air Force Office of Scientific Research and National Science Foundation

A new theoretical self-consistent-field model has been developed for calculating the localized electronic states of impurities in crystals. This method has the advantage over other theoretical techniques, that it does not require an explicit calculation of the electronic band-structure spectrum for the perfect crystal. Because the impurities and atoms of the host lattice are treated on an equal basis, one can easily

set up the model for multiple impurities and neighboring atoms forming clusters, lines, or planes in the crystal. The model is being applied to semiconductors and insulators containing transition-metal impurities which produce localized electronic states lying deep within the valence-band conduction-band gap. A spin-polarized version of the model is also being set up for the investigation of magnetic impurities in metals and alloys, in particular those for which the Kondo effect has been observed.

21.0 Theory of Chemisorption by Transition Metals

Personnel: K. H. Johnson

Sponsorship: National Science Foundation

We have developed a self-consistent-field theory for the chemisorption of atoms and small molecules by transition metals. The theoretical model permits a calculation of the electronic energies and charge densities associated with the localized bonding between the chemisorbed species and transition-metal substrate. Exchange splitting and spin-polarization are essential features of the model. We are particularly interested in treating those cases (e.g., carbon monoxide chemisorbed on nickel) where there is some experimental evidence for the formation of "surface molecular compounds". It is hoped that this theoretical approach will lead to a quantitative understanding of the relationship between chemisorption and catalysis by transition metals. Applications to biochemisorption and biocatalysis by transition metals in enzymes (e.g., hemoproteins) are also planned.

22.0 Nature of the Chemical Bond in Complex Materials

Personnel: K. H. Johnson; F. C. Smith, Jr.

Sponsorship: National Science Foundation and Air Force Office of Scientific Research

Many of the most complex forms of matter may be considered to be built up large numbers of periodic or aperiodic clusters of several atoms or more. As examples we may cite ordered molecular crystals with many atoms per unit cell, disordered or amorphous solids, and composite materials.

There is much current interest in developing quantitative theories for the chemical bonding and related properties of such systems. We have recently developed a cluster model for calculating the electronic structures of complex solids from first principles. The model is based on a combination of our scattered-wave approach to molecular structure with standard methods of band theory. This approach is particularly useful for establishing, within the framework of the model, the degree to which the electronic band structure and density of states of the material are determined by the nature of the short-range chemical bonding of component "molecular" clusters. Applications to ordered crystals of the pyrite structure, with 12 atoms per unit cell, have been completed. Applications to amorphous materials are in progress.

Theses:

R. Currat, "X-Ray Investigation of the Electronic Momentum Distribution in Beryllium Single Crystals", Ph.D., Department of Metallurgy and Materials Science, August, 1969.

M. Kuninsky, "Photoconductivity in Thin Films of Amorphous Selenium", M.S., Department of Physics, August, 1970.

S. Lee, "X-Ray Studies of Aqueous HCl Solutions", M.S., Department of Metallurgy and Materials Science, August, 1969.

J. Linderman, "Design for a Teacher-Interactive CAI System", M.S., Department of Electrical Engineering, June, 1970.

K. R. Morash, "Magnetic Neutron Scattering from MnO Single Crystals", Ph.D., Department of Metallurgy and Materials Science, August, 1969.

M. D. Rechtin, "Critical Scattering in CoO", Ph.D., Department of Metallurgy and Materials Science, May, 1970.

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K. H. Johnson, and F. C. Smith, Jr., "Bands, Bonds, and Boundaries", Proceedings of the IBM Conference, Computational Methods in Band Theory (Plenum Press, 1970).

II PHYSICAL METALLURGY - Phase transformations, Metastable Phases, Diffusion, Structure-Property Relationships, Strengthening Mechanisms, Plastic Deformation

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Sponsorship

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Air Force Materials Laboratory, Contract F33615-69-C-1603, DSR 71596

Bethlehem Steel Corporation, DSR 70391

Climax Molybdenum Company, 21836

Office of Naval Research, Contract No. N00014-67-A-0204-0027, DSR 71362

NDEA Traineeship

NSF Traineeship

NASA Traineeship

1.0 Strain-Enhanced Diffusion

Personnel: M. Cohen

Sponsorship: None

The enhancement of self-diffusivity during plastic deformation has been quantitatively explained on the basis of "pipe" migration along moving dislocations. It now seems likely that the diffusivity of interstitial atoms, such as that of carbon in body-centered cubic iron, can also be increased by furnishing extra dislocation paths. The indications are that enhanced interstitial diffusion should result from the segregation of carbon atoms to dislocations and also from a lowering of the migration energy due to the dislocation stress field.

2.0 Nucleation of Martensitic Transformations

Personnel: M. Cohen; V. Raghavan and M. K. Korenko

Sponsorship: Office of Naval Research

Models have been developed to take autocatalytic and partitioning effects into account in isothermal martensitic transformations, particularly in iron-nickel and iron-nickel-manganese alloys. A critical factor in determining the associated nucleation rates is the mean volume per martensitic plate, which is now found to be a function of the reaction temperature. Quantitative metallography is being applied to this problem.

Small-particle experiments are underway to minimize the autocatalytic effects and to concentrate on the initial rate of nucleation resulting from the pre-existing nucleation sites in the parent phase. These embryos are subject to control by exposing the parent phase to high magnetic fields prior to

martensitic transformation.

Calculations are being carried out to estimate the stresses, arising from the chemical driving force, that are available to trigger-off a martensitic embryo.

3.0 Mössbauer Investigations of Iron-Base Interstitial Phases

Personnel: M. Cohen, in collaboration with R. Kaplow; W. K. Choo
Sponsorship: Office of Naval Research

Virgin martensites have been produced in very high-carbon iron-carbon martensites by splat quenching in an effort to determine through Mössbauer spectroscopy whether the trapped carbon atoms are randomly arranged or clustered. Further resolution of the Mossbauer peaks has now revealed additional detail for interpretation. Progressive changes on aging from the liquid-nitrogen temperature up into the usual tempering range are under study.

These Mössbauer measurements will be extended to iron-nickel-carbon martensites.

4.0 Order-Disorder Phenomena in Iron-Carbon Martensites

Personnel: M. Cohen; A. M. Sherman
Sponsorship: Climax Molybdenum Company of Michigan

The relationship between tetragonal and cubic martensites is being studied with reference to the distribution of carbon atoms. A key issue in the current picture is whether the cubic form of martensite represents a disordered array of the interstitial carbon atoms, thus eliminating the tetragonal structure corresponding to the ordered configuration, or whether the martensite simply becomes depleted by virtue of carbon movement to dislocations and other structural traps. Experiments have been devised with iron-nickel-carbon alloys to distinguish between these alternatives, and to check the prevailing order-disorder theories.

5.0 Martensitic Transformations in Iron Alloys

Personnel: J. F. Breedis, in collaboration with L. Kaufman (ManLabs Inc.)
Sponsorship: Advanced Research Projects Agency

The formation of the hexagonal close-packed (ϵ) and body-centered cubic (α) structures in pure iron under high pressure conditions, as well as the morphological and crystallographic aspects of martensitic transformation to these structures at atmospheric pressure in iron alloys, has been reviewed. It is concluded that the unique features of α- or ϵ-martensite formation are not dependent upon the presence of the ϵ-phase. Application

of the phenomenological theory of martensitic transformation has not successfully rationalized the crystallography of lath-martensite. The criterion for ϵ - and α-phase formation is established using the regular solution approximation and appropriate lattice stability parameters. In particular, the ϵ-phase can be formed in Fe-Ni-Cr compositions through stress-induced transformation attending α-martensite formation. Further consideration suggests that the $\epsilon \rightarrow \alpha$ transformation is not expected at atmospheric pressure at temperatures below approximately 500° K in the alloys considered. Thus, two martensitic transformations, $\gamma \rightarrow \epsilon$ and $\gamma \rightarrow \alpha$, can occur jointly in certain alloys.

6.0 Massive Transformations in Alloys

Personnel: M. Cohen; R. K. Mehrotra

Sponsorship: Office of Naval Research

Silver-cadmium alloys of approximately 50-50 composition exhibit a massive transformation below 200° C. This system is being used to provide a further test of the model proposed by D. A. Karlyn, J. W. Cahn and M. Cohen. The measurements thusfar indicate linear growth rates without any detectable delay times, the latter being in contrast to the observations on copper-zinc alloys. This difference points to further refinements in the model.

7.0 Strengthening Mechanisms

Personnel: M. Cohen; G. T. Eldis and F. B. Fletcher

Sponsorship: Office of Naval Research, Bethlehem Steel Corporation

The strengthening and aging characteristics of virgin martensites in iron-nickel-carbon and iron-nickel-molybdenum-carbon alloys are being investigated. An important stage of strengthening has been encountered, straddling room temperature, which is accompanied by a significant increase in electrical resistivity. Carbon clustering prior to actual carbide precipitation is one of the hypotheses being tested to account for these phenomena. These effects appear to be clearly revealed only in virgin martensites, and are obscured in regular martensites which form above room temperature.

The strength-differential effect is being examined in a series of iron-nickel-carbon steels, designed to provide a wide range of carbon contents and full martensitic hardenability. Preparations are also underway to determine the temperature-dependence of the strength-differential in these alloys.

8.0 Strengthening Mechanisms in Titanium Alloys

Personnel: J. F. Breedis; D. S. Gelles and W. D. Rosenberg

Sponsorship: Air Force Materials Laboratory

National Science Foundation Fellowship

The objectives of this research program are to investigate the strengthening of beta titanium alloys through: (1) precipitation of the omega phase and spinodal decomposition, (2) additions of interstitial solutes,and (3) martensitic transformation induced by quenching or deformation. Ternary Ti-Nb-Me alloys have been prepared on the basis of regular solution thermodynamic calculations to study strengthening by spinodal decomposition. The conclusion of this effort is that while phase separation is expected in many beta alloys, more stable intermetallic compounds and the omega phase form to preclude spinodal decomposition. Present efforts are directed towards the strengthening of beta alloys by omega formation. Omega has been found to increase drastically the rate of work hardening in titanium-vanadium to result in ductile failure of beta at very low or negligible elongations. Strengthening without loss of all ductility appears possible by control of the perfection and volume fraction of omega phase. Titanium-molybdenum-oxygen alloys have also been prepared to study in particular the strength-differential effect and interstitital solute-dislocation reactions in beta and martensitic structures.

9.0 Strain Hardening at Very Large Plastic Deformations

Personnel: M. Cohen, J. F. Breedis; C. Biswas, A. M. Sherman

Sponsorship: Office of Naval Research

The strain hardening of iron-base and titanium-base alloys during severe plastic deformation by wire drawing are being investigated from the standpoint of the mechanisms involved. For the ferrous materials, the main strengthening process is one of cell formation within the grains, and the progressive refinement of the cells. Cell formation in hexagonal close-packed titanium is less pronounced, and a different strain-hardening process may be operating. However, body-centered cubic titanium-molybdenum alloys will also be studied and compared with the strain-hardening of iron.

The dynamic recovery occurring during the wire drawing of iron appears to be mechanically activated rather than thermally activated. This recovery phenomenon involves cell-wall migration and cellular coalescence, thus detracting from the cellular refinement that normally occurs during plastic deformation. The temperature-dependence of this recovery process is being studied.

10.0 Deformation of Face-Centered Cubic Metals to Very-High Strains

Personnel: J. F. Breedis, in collaboration with M. B. Bever; J. W. Pugh

Sponsorship: Advanced Research Projects Agency

Limited information is available on the structure-properties relations for nickel, copper, austenitic iron-nickel and gold-silver alloys. These investigations however, have concentrated on the measurement of the hardness or other strength properties as functions of strain mostly without correlation to structural features. Copper and two copper-aluminum alloys, which have large differences in stacking fault energy and dislocation substructures after deformation, are being strained to 800 percent. Mechanical properties are to be correlated with transmission microscopy observations and measurements of stored energy.

11.0 Deformation of Ruthenium Single Crystals

Personnel: J. F. Breedis and D. B. Snow

Sponsorship: Advanced Research Projects Agency

The influence of axial ratio, elastic anisotropy, and stacking fault energy on the choice of slip modes in HCP metals has received considerable attention. However, the correlation of mechanical behavior with dislocation configurations in single crystals of low-axial-ratio HCP metals has been of less concern. The present study is being conducted to examine in detail the dislocation substructures associated with prism slip in ruthenium, to correlate this structure with observed mechanical behavior, and to compare this information with that known for HCP metals having similar axial ratio and slip systems.

In marked contrast to titanium, zirconium, and beryllium, dislocation structures after prism slip in ruthenium contain pronounced edge braids rather than the arrays of screw dislocations found in the three former metals. Thus, the dislocation structure in ruthenium is nearly identical with that found in magnesium which deforms by basal slip. The observations suggest a model for work hardening which involves the annihilation of screw dislocations with mutual trapping of edge dislocations.

Consideration is presently being given to the importance of elastic anisotropy and stacking fault energy to the deformation behavior of ruthenium in an effort to rationalize its characteristics relative to titanium and magnesium.

12.0 Fatigue of Titanium Alloys

Personnel: J. F. Breedis and R. Stevenson

Sponsorship: Advanced Research Projects Agency

The cyclic hardening behavior of polycrystalline alpha-titanium and titanium alloys is being studied. A conventional tensile machine has been modified to permit push-pull stress cycling between specified limits of plastic strain. Incorporated into the system is the capability of displaying mechanical hysteresis loops and the ability to suppress part of the load scale when desired to evaluate more clearly the attainment of saturation. The variables of grain size, plastic strain amplitude and composition are being studied with correlation of the mechanical behavior with dislocation structures developed during cyclic stressing.

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J. F. Breedis and L. Kaufman, "Formation of HCP and BCC Phases in Austenitic Iron Alloys," Metallurgical Transactions, accepted for publication.

D. B. Snow and J. F. Breedis, "Deformation of Ruthenium Single

Crystals," Proceedings, Second International Conference on the Strength of Metals and Alloys, accepted for publication.

M. K. Koul and J. F. Breedis, "Phase Transformations in Beta Isomorphous Titanium Alloys," Acta Metallurgica 18 579 (1970).

M. K. Koul and J. F. Breedis, "Omega Phase Embrittlement of Titanium Alloys," Metallurgical Transactions 1 1451 (1970).

III PHYSICAL METALLURGY - Solid-State Kinetics

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M. J. Richards, Research Assistant

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R. B. Heady, now with Shell Development Company, Emeryville, Calif.

J. Weins - Has not accepted permanent employment

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C. P. Biswas, Research Staff, MIT

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R. B. Heady, Ph. D., Metallurgy and Materials Science, February 1970
J. Weins, Ph. D., Metallurgy and Materials Science, June 1970
J. M. Wells, Sc. D., Metallurgy and Materials Science, February 1970
C. P. Biswas, S. M., Metallurgy and Materials Science, September 1970
J. C. Baker, Ph. D., Metallurgy and Materials Science, June 1970

Sponsorship:

National Science Foundation, GK-10586, DSR 71384
Advanced Research Projects Agency, SD-90, DSR 75129, 72229
National Institutes of Health, DE02384-04, DSR 71552

Research Report

1.0 Theory of Spinodal Decomposition

Personnel: J. W. Cahn
Sponsorship: National Institutes of Health

A theoretical basis for selecting ternary additions to raise or lower the reaction temperature for spinodal decomposition in binary alloys was established as part of a continuing study on multi-component systems. The study further predicted that ternary phases could be unstable to spinodal decomposition and ordering simultaneously, an untenable possibility in binary alloys. A simple construction based on binary interaction coefficients were also used to estimate the start temperatures for these reactions. This treatment differed from previous work chiefly by the inclusion of coherency strain energy which tends to stabilize phases. Future work will use the above concepts in attempts to control the age-hardening behavior of gold-nickel base alloys.

2.0 Electron Irradiation of BCC Metals

Personnel: K. C. Russell; J. M. Wells, R. Powell, K. Mino
Sponsorship: Advanced Research Projects Agency, National Science Foundation

J. Wells has completed his investigation of the stage I annealing kinetics of irradiated iron wires. The substages characteristic of Frenkel pair

annihilation were observed. However, the observed activation entropies for annihilation were much larger than predicted by the usual migration models.

We have modified the cryostat to allow higher electron irradiation fluxes and better temperature control during annealing. R. Powell and K. Mino are presently verifying and extending Wells' investigation. If his results prevail, we will have to reshape our thinking about the nature of low-temperature recovery from radiation damage.

3.0 Growth Enhancement of Ice Crystals

Personnel: J. Goldman
Sponsorship: National Science Foundation

It is known that when ice solidifies from aqueous solutions, large potentials of the order of hundreds of volts may develop across the solid-liquid interface. This phenomenon is probably responsible for the growth rate enhancements over values for pure water that have been observed. The present research is concerned with evaluating the effects of potential differences on the growth of ice.

4.0 Thermodynamics of Solids Under Non-Hydrostatic Stress

Personnel: F. Larche
Sponsorship: National Science Foundation

The theoretical condition of equilibrium of multi-component solids under non-hydrostatic stress is being investigated. Systems where constraints are imposed on the possible movements of atoms on the lattice are considered. As a future development, this work should lead to the formulation of a diffusion equation for specimens under stress.

5.0 Coarsening in Solid State Transformations

Personnel: K. C. Russell and S. Bha''acharyya
Sponsorship: National Science Foundation

We have developed a theory of coarsening (Ostwald ripening) for sparingly soluble compound precipitates such as oxides dispersed in a metal. Small changes in composition or atmosphere may change the coarsening rate by several orders of magnitude. Also, as many as four or five activation

energies may characterize coarsening, depending on composition, atmosphere, and relative value of the atomic mobilities. S. Bhattacharyya is presently testing this theory in a series of experiments on Cu alloys containing dispersed SiO_2 particles.

6.0 Kinetics of Disorder-Order Transitions

Personnel: M. J. Richards
Sponsorship: National Science Foundation

We are investigating the kinetics of disorder-to-order transitions. In conjunction with Mr. Boswell the "pulse-heater" has been rebuilt to allow heat treatments from 0-5000 milliseconds. The system Iron-Palladium has been chosen for study.

7.0 Non-Equilibrium Solidification

Personnel: J. Baker
Sponsorship: National Science Foundation

Solidification under conditions far from equilibrium can lead to a spontaneous increase in the chemical potential of the minor component of a binary alloy. Such an experimental result is not inconsistent with thermodynamics, yet there are "thermodynamic" theories that begin by postulating that such solute trapping can't happen. A theoretical and experimental program is aimed at comprehending the nature of the irreversible processes.

8.0 Liquid Phase Sintering

Personnel R. B. Heady and J. W. Cahn
Sponsorship National Science Foundation

The capillary forces between particles due to the presence of a liquid phase have been analyzed. Contact geometrics are predicted to have a marked effect on the kinds of interparticle forces and how these depend on liquid volume. The normal force between two spheres is a maximum at infinitesimal liquid volumes, while for the corner-on-plane geometry it is zero and increases rapidly with volume. Sphere contacts have only normal forces, while contacts among jagged particles give rise to shears and torques which are likely to be important in particle rearrangement leading to densi-

fication.

9.0 Nucleation Near a Critical Unmixing Point in a Binary System

Personnel: R. B. Heady
Sponsorship: National Science Foundation

To test nucleation theory critical undercooling has been measured in a system in which the thermodynamic functions are known.

10.0 Thermodynamics Near a Critical Unmixing Point in a Binary Liquid System

Personnel: R. B. Heady
Sponsorship: National Science Foundation

Vapor pressure has been determined near the consulate point in the perfluorocyclomethylhexane-cyclomethylhexane system. The thermodynamics functions deviate markedly from those of a regular solution. The scaling law exponents β and γ' have been determined to be $\beta = .33$, $\gamma' = 1.3$.

11.0 Fast Reactions in Solids

Personnel: P. Boswell and K. C. Russell
Sponsorship: National Science Foundation

The so-called massive transformation of a $\beta \rightarrow \alpha$ brass takes place at velocities the order of cm/sec, as opposed to the microns/hour velocities characteristic of ordinary solid state reactions. Hawbolt and Massalski, and Ayers and Massalski have disputed the theory of Karlyn, Cahn and Cohen, which predicts massive growth mainly in a single-phase region and claim to have obtained the massive transformation in the two-phase $\alpha + \beta$ region of the phase diagram. We have utilized our double-bank capacitor-discharge pulse heater to initiate massive growth in the single phase alpha region, followed by a pulse into the two phase region. Within the ± 2 degrees C accuracy of the experiment, the massive reaction ceases at the $\alpha/\alpha+\beta$ boundary.

We are now proceeding to a study of reversion kinetics in Al-4% Cu. This reaction is essentially complete in less than one second, but the pulse heater permits detailed study for reaction times of millisecond duration.

12.0 Nucleation Kinetics

Personnel K. C. Russell, C. Biswas and P. Engel
Sponsorship National Science Foundation, Advanced Research Projects Agency

C. Biswas has completed his investigation on the precipitation of a Co-rich phase from a Cu-rich Cu-Co alloy. He found that observed precipitation rates on grain boundaries, dislocation lines and on random lattice sites were in good agreement with the theories of nucleation for these phenomena. This agreement justifies increased confidence in the predicative power of nucleation theory.

The driving force for nucleation is a vital, but seldom known factor in the nucleation rate equation. K. Russell (in association with Drs. H. Aaronson and K. Kinsman of the Ford Scientific Laboratory) have developed equations for obtaining this quantity from solution models and phase diagram data.

It is widely recognized that unstable quenched-in defects may catalyze nucleation reactions. We have derived kinetic and thermodynamic criteria for such embryos to be effective catalysts.

13.0 Nucleation of Voids

Personnel: K. C. Russell
Sponsorship: National Science Foundation, Advanced Research Projects Agency

Radiation induced void formation in reactor materials has become an unexpected and major obstacle to the development of high-flux nuclear reactors. The irradiated materials may have substantial steady-state concentrations of vacancies, solvent interstitials, helium interstitials and helium-vacancy complexes. Further, as the complexes are not necessarily in equilbrium with the vacancies and He atoms, detailed balancing is not directly applicable. These problems have been overcome and the formalism of linked flux analysis was used to derive a rate equation for void nucleation under reactor conditions. One may use this expression to predict the effects of such variables as temperature, defect concentrations, surface tension and internal and external pressures on void nucleation rates. Thus, design criteria may be developed to minimize void formation.

Theses: (All in the Department of Metallurgy and Materials Science)

R. B. Heady, "An Experimental Investigation of Nucleation Theory in a Liquid-Liquid Miscibility Gap", Ph. D. Thesis, September 1969.

J. M. Wells, "Stage I Recovery in Electron-Irradiated Iron", Sc. D. Thesis, January 1970.

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J. J. Weins, "The Effect of Spatial and Particle Size Distributions on Coarsening Rates", Ph. D. Thesis, June 1970.

J. Baker, "The Theory of Solidification", Ph. D. Thesis, June 1970.

Publications:

D. A. Karlyn, J. W. Cahn, and M. Cohen, "The Massive Transformation in Copper-Zinc Alloys", TMS-AIME, 245, 197 (1969).

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K. C. Russell, "The Role of Quenched-In Embryos in Solid-State Nucleation Processes", Accepted by Metallurgical Transactions.

P. Boswell and K. C. Russell, "Massive Transformation in a Two-Phase Region", (to be submitted to Metallurgical Transactions.

H. Matyja, B. C. Giessen, K. C. Russell, and N. J. Grant, "An Electron Microscope Study of the Precipitation of Silicon from Splat-Cooled Al-Si Alloys", (to be submitted to Metallurgical Transactions.

IV. HIGH TEMPERATURE METALLURGY

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Degrees granted:
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H. M. Dalal, Sc. D., Metallurgy and Materials Science, June 1970
R. M. Davison, Sc. D., Metallurgy and Materials Science, June 1970
K. E. Erhardt, Sc. D., Metallurgy and Materials Science, June 1970
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Sponsorship:
Aeronautical Systems Division, Wright-Patterson AFB, F33615-67-C1441, DSR 70324
National Aeronautics and Space Administration, NGL 22-009-003, DSR 76243
International Copper Research Association, Inc., DSR 71535
Advanced Research Projects Agency, SD-90, DSR 78887, DSR 71625
Advanced Research Projects Agency, DAHC15-70-C-0283, DSR 72543, DSR 72542

Research Report

1.0 Dispersion Strengthening

Personnel: N. J. Grant, W. Schilling, M. Grewal, D. Kenton, V. Sarin
Sponsorship: National Aeronautics and Space Administration and International Copper Research Association

Using finely atomized nickel-base powders containing an oxidizable element such as Al or Be, comminuting to near micron thick flakes, a coating of Al_2O_3 or BeO is formed. Further oxide formation is possible by reaction of the non-refractory matrix oxides with Al or Be in solution, by internal oxidation. Excellent low and high temperature properties have been obtained.

To take advantage of the contribution of bonding energy between matrix and hard particle dispersoids, nickel base alloys containing titanium have been internally carburized. Other nickel base alloys have been prepared by mechanical blending of finely attritted nickel base powders (containing Cr for oxidation resistance) with sub-micron TiC powders. Very high strength values have been achieved at room and intermediate temperatures with

interesting stress rupture properties at 1000 degrees C (100-hour life at 5500 psi).

Copper-zirconium alloys, inert gas atomized (-150 micron size), steam atomized (-2000 micron size), and metal disc splat cooled (flakes), are being compacted by hot extrusion and tested for strength, ductility, formability, and electrical conductivity. Refinement of structure by use of quenched powders permits a higher zirconium content alloy to be made with improved low temperature properties. In particular, excellent retention of structure and property stability after exposure for one hour at 700 degrees C has been observed.

2.0 Structure and Property Control by Rapid Quenching (Splat Cooling of Liquid Metallic Solutions

Personnel: N. J. Grant, C. Jansen, J. Vitek, M. Lebo

Sponsorship: National Aeronautics and Space Administration

Mrs. Jansen is studying the decomposition of metastable solid solutions of aluminum supersaturated with transition metal elements (Cu, Mn, Fe, Ni, Co) by means of X-ray diffraction and transmission electron microscopy. Alloy foils are produced by the splat cooling technique in which a molten metal charge is quenched at rates of 10^7 to 10^9 degrees C/sec. The maximum solute content has been increased by as much as 20X (e.g. Fe in Al). These highly supersaturated foils are examined immediately after quenching by X-ray diffraction and transmission electron microscopy. The change of the lattice spacing is measured by X-ray diffraction as a function of the annealing time to follow the precipitation kinetics. Examination of these alloys for age-hardening response and dispersion strengthening effects is a prime aim of the program.

A detailed review of the recent work on amorphous structures produced by splat and vapor cooling was completed by Mr. Vitek. The splat cooling equipment is being updated to provide for higher melting temperatures and multiple splat production.

Mr. Lebo has been studying an aluminum - 7 weight percent silicon alloy which has been splat cooled and extruded at 300 degrees C and a 20:1 extrusion ratio. The resultant structure consists of a uniform distribution of sub-micron primary silicon particles. A study of tension and stress rupture properties as a function of silicon size and distribution will now be performed.

In addition, a commercial aluminum alloy, 2024, has been splat cooled to coarse flakes and extruded at 300 degrees C and a 20:1 extrusion ratio. Compared to ingot material, in which intermetallic phases up to 20 microns lead to poor fatigue life, the near micron particles now contribute to the strength of the alloy, with no loss of ductility. Fatigue life is increased by 5 to 7 X over ingot product. Further refinement of the structure to break down surviving powder particle boundaries is under way. Tension, fatigue, and stress rupture tests are in progress.

3.0 Deformation and Fracture at High Temperatures at High Strain Rates

Personnel: N. J. Grant, R. M. Pelloux, G. Campbell, N. Cederblad

Sponsorship: Advanced Research Projects Agency

Mr. Campbell is studying the variables controlling recrystallization during the hot working of austenitic, cast and hot isostatically pressed 18-8 stainless steel. Included in these studies are the effects of deformation temperature, amount of strain, strain rate, initial grain size and holding time at temperature between increments of strain. Following these studies, efforts will be undertaken to achieve maximum rates of grain refinement and to establish the role of the refined grain size, hot plasticity, and room temperature tension properties.

Similar studies have been initiated on a nickel base superalloy.

4.0 Corrosion Fatigue

Personnel: R. M. Pelloux, J. Cooper

Sponsorship: Advanced Research Projects Agency, Air Force Materials Lab.

The corrosion fatigue resistance of Al-Zn-Mg aluminum alloys (7075) in a sea water environment was studied as a function of the aging heat treatment. The S-N curves were obtained for three aging conditions: 1) underaged; 2) peak aged; 3) overaged alloys in dry nitrogen, in air, and in sea water. There is no significant difference in the sea water corrosion fatigue strength between the three aging treatments, which is in contrast with the stress corrosion resistance in the overaged condition.

Fatigue tests on precorroded samples immersed for varying times in salt solution indicated a higher susceptibility to pre-fatigue damage for the

underaged alloys. However, after eight days of precorrosion all the alloys have the same fatigue strength. Extensive Stage I cracking is observed in all specimens indicating an increased surface slip activity in the presence of the sea water environment.

A new program to study the influence of a corrosive environment on the mechanisms of fatigue crack propagation has been initiated.

5.0 Fatigue Mechanisms in Aluminum Alloys

Personnel: N. J. Grant, R. M. Pelloux, A. Wilson, K. Erhardt

Sponsorship: Air Force Materials Laboratory

A detailed evaluation by scanning electron microscopy of the characteristic fatigue fracture features in aluminum alloys was completed during the last year. The fracture features previously identified by means of replicas were vonfirmed, however, the SEM gives a more realistic view of the complexity of the fracture processes. The extensive amount of secondary cracking revealed by the SEM is not fully accounted for at this time. Stage I fatigue cracks were clearly identified with the SEM. Inclusions and other hard phases serve as crack initiation sites but do not seem to interfere with the shear mode of crack propagation typical of Stage I.

The influence of cycling rate and temperature on fatigue crack propagation in 2024 T3 alloys was investigated at 80 and 3000 degrees F and at 600 cpm and 10 cpm. There is no rate effect at low or high temperature but the growth rate is strongly dependent upon the propagation direction (transverse or longitudinal) because of the distribution of the inclusions.

Efforts to grow some single crystals of 7075 alloy by directional solidification and strain anneal techniques have so far yielded only large grained specimens. Measurements of crack tip opening displacements as a function of K are in progress. The crack tip openings of specimens kept under load are measured by scanning electron microscopy.

6.0 Cobalt Base Superalloys

Personnel: N. J. Grant, R. Robinson

Sponsorship: American Metals Climax Company

Powder techniques, utilizing coarse powders quenched at high rates, are

being studied to determine how much of an increase in volume content of carbide (HfC) it will be possible to incorporate in the alloy while retaining ductility and toughness. The program will permit wide variations of the alloy content of the matrix to achieve the best balance of strength, alloy stability at high temperatures, and oxidation resistance.

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N. J. Grant: "Powder Metallurgy", Research and Development, August 1970, 59.

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Sponsorship:

* Advanced Research Projects Agency SD-90, DSR 72222, 72226, 72266

National Aeronautics and Space Administration, NCR22-009-125, DSR 76335

National Science Foundation GK-1653, DSR 71474

National Aeronautics and Space Administration, NGR22-009-517, DSR 72055

North American Philips DSR 72120

IBM 21894

Research Report

1.0 Semiconductor Surfaces

Personnel: H. C. Gatos, A. F. Witt, C. L. Balestra, J. J. Daniele, S. Spitzer

Sponsorship: National Aeronautics and Space Administration

The work was aimed at the electronic configuration of semiconductor surfaces and was pursued along two main directions: the study of the silicon-oxide interface and the study of cadmium sulfide surfaces.

The silicon-oxide interface was employed as a vehicle for developing a tunneling spectroscopic technique applicable to metal-insulator-semiconductor (MIS) configuration. For this purpose the theory of the metal-insulator system was modified and adopted for MIS structures. Special techniques were developed for the preparation of aluminum-silicon dioxide-silicon devices. The key step was the preparation of thin oxide layers (about 100 Å thick) capable of withstanding electric fields exceeding 5×10^6 V/cm. Such layers, were achieved by a low temperature nitric oxide treatment. Silicon surfaces with the <111> orientation were employed. All measurements were carried out at room temperature. It was shown that tunneling spectroscopy can yield results on the type of the semiconductor (n- or p- type), on the surface potential, surface charge and surface state distribution. The results on the (111) silicon surfaces were found consistent with those obtained by other techniques and extended our insight into the distribution of surface states along the entire energy gap.

In studying the cadmium sulfide surfaces a circuitry for continuous measurement of contact potential of semiconductor surfaces was designed and constructed with a resolution of 1 mV. Contact potential measurements were carried out on cadmium sulfide surfaces cleaved in ultrahigh vacuum (approximately 2×10^{-11} torr) at room temperature. The cleaved surfaces were found to be essentially insensitive to light and pure oxygen (changes in contact potential less than 25 mV were found). However, preliminary results indicate that water vapor (about 10^{-8}) interacting with oxygen and light had substantial effects bringing about changes in contact potential of 0.1 to 1 volt.

2.0 Semiconductor Thin Films

Personnel: H. C. Gatos, A. F. Witt, M. Lichtensteiger, S. Minagawa
J. Mroczkowski, A. Vejux, B. Wessels

Sponsorship: ARPA, North American Philips

Our research on semiconductor thin films was continued along three experimental approaches; sputtering, direct evaporation and vapor transport.

The work on sputtering was concentrated on the preparation of cadmium sulfide films of improved crystalline and chemical perfection. P-type films reported previously to be unstable with time became less p-type . The reasons for such instability are not clear at present. A study of the effect of the substrate temperature (up to 500°C) on the cadmium sulfide films was initiated. At the high temperature range it was found that the films had the highest resistivities ever observed, of the order of 10^8 ohm-cm. Their electrical and optical characteristics resembled those of thin cadmium sulfide crystals prepared by vapor transport methods. Sputtering in doping ambients (such as PH_3 and H_2S) is being continued.

Research on controlling the parameter of the direct evaporation of cadmium sulfide films was continued. An evaporation source was designed which consists of tantalium tubing with 0.0135" opening; it is resistance heated and monitored by an oscillating crystal sensor. Quite steady deposition rates were achieved in the range of 50 to 200 Å/sec. Control of substrate temperature was also developed for temperatures ranging from 4.2°K to 250-400°C depending on the materials used as substrate. For the crystalline characterization of these films a double-crystal x-ray diffractometer was employed with a dislocation-free germanium single crystal as the monochromator. Typically, a 2μ thick film, deposited on glass at 150°C gave a rocking curve with 8° half-width. Although the use of single crystal substrates (Ge, CdS) had no effect on the half-width of the rocking curves, heat treatment of the films with post-deposition of silver (Sakenberghe method) has decreased the half-width to 3.5°C.

A number of methods (light microscopy, scanning electron microscopy and others) were studied for the determination of the thickness of SiC film deposited on single crystal SiC substrates by vapor transport (silane and propane). The only successful method was based on employing substrates of different conduction type than the deposits. The deposits were leveled and the p-n junction (origin of the deposit) was located by a thermoelectric probe. On the basis of this method it was found that the growth rates

were significantly lower than those calculated. Furthermore, no other condensed phase (silicon or graphite) was found even when such conditions were supposed to be present according to thermodynamic computations. The growth rate was found to increase monotonically from zero to about 10 μ/hr at 1600°C with increasing silane concentration from 2×10^{-4} to 1.5×10^{-3} atm at a carbon to silicon ratio in the feed gas equal to unity. Similarly the growth rate increasedmonotonically with increasing propane concentration provided the silane pressure was kept constant. An apparatus was constructed for the electrical characterization of the deposits (resistivity and Hall coefficient) for temperatures ranging up to 900°C.

3.0 Amorphous Semiconductor Materials

Personnel: H. C. Gatos, A. F. Witt, N. Platakis, K. Owyang
Sponsorship: ARPA, IBM, General Telephone and Electronics

In the vitreous system $(1-x)As_2Se_3 \times Sb_2Se_3$ the devitrification, the switching and memory phenomena were investigated.

The devitrification studies were undertaken since parameters such as the growth rate of crystals in a vitreous matrix, the time required for the first crystal to appear, the related activation energies, and the compositional changes occuring during the devitrification are important in attempting to understand phenomena related to the switching and memory devices based on vitreous materials. The devitrification studies included: Measurement of the growth rate of relatively large crystals in a vitreous sample as a function of temperature and composition. Measurements of the time required for the first crystal to appear (visible under magnification 570x) when a vitreous material was heated at a constant temperature. Morphology of the crystals grown in a devitrifying sample. Compositional changes resulting from the growth of crystals in the vitreous samples. In these experiments the activation energies of growth of relatively large crystals and the devitrification activation energies at the initial stage of devitrification were determined. The light source of a metallographic microscope was used as the heat source. The temperature was measured by bringing the junction of the imbeded thermocouple (25μ) into focus. The desired temperature was achieved by changing the aperture diaphram setting. Temperatures ranging from 23°C to 190°C could be obtained. The activation energy for growth in samples of the composition with x = 0.1 was found to be 38 kcal/mole. For

the samples of the compositions with x = 0.3, 0.4, 0.5 the activation energy was independent of the composition and had a value of about 50 kcal/mole. At 373°K the growth rate along the length of the crystal was 2 x 10^{-6} μ/sec for specimens with the composition x = 0.1, 5 x 10^{-5} μ/sec for x = 0.3, 0.4 and 7 x 10^{-4} μ/sec for x = 0.5. The rate of growth was three times greater along the length than along the width of the growing crystal, at 373°K. The activation energy for the first crystal to appear was found to be 12 kcal/mole for the composition with x = 0.1 and about 55 kcal/mole for x = 0.3, 0.4, 0.5. Crystals grown in glassy samples with the composition x = 0.1 had a dendrite morphology, while those grown in samples with the x = 0.3, 0.4, 0.5 had a common morphology with more or less a rectangle shape. At high temperature (190°C) the crystals grown in samples with x = 0.3, 0.4, 0.5 were needle like. Electron microprobe analysis and scanning electron microscopy revealed that the crystals grown during devitrification had slightly higher Sb concentration than the surrounding vitreous matrix. In contrast, crystals grown during the liquid to solid transition were very rich in Sb relative to the surrounding matrix. Concerning the switching and memory phenomena, bulk and thin films (flash evaporated) were employed. Preliminary measurements on devices with the compositions x = 0.3 and 0.4 indicated that the threshold switching occurs both in bulk form and in films. The threshold voltage of the former is much higher than the latter. There was a recovery period of 5 - 10 sec. after each switching operation, in the course of which the original threshold voltage was fully restored. This observation is consistent with the prediction of the double injection model proposed by Hensich and Ovshinsky (J. of Non-Crystalline Solids, 4, 1970, p. 38). The recovery period was taken as the gradual decay of the trapped carrier population after the return to the off state. A study of the voltage-current characteristics and the threshold voltage as a function of composition and temperature is underway.

4.0 Semiconductor Growth and Characterization

Personnel: H. C. Gatos, A. F. Witt, M. Lichtensteiger, K. M. Kim, G. Galyon, J. M. Sandor, R. Singh, D. C. Miller, F. T. Endicott, E. Eser

Sponsorship: ARPA, NASA, NSF

4.1 Growth and Characterization of the Pseudo-Binary System GaSb-InSb.

The applicability of the Czochralski technique to the growth of GaSb-InSb single crystals was investigated. It was found that only up to 15 mol.% InSb can be incorporated into a single crystal GaSb matrix. Beyond 6 mol.% InSb, severe cracking due to thermally generated stresses at the crystal surface imposes limitation on this approach. High temperature Hall measurements led to a determination of the relative position of the three conduction band minima, <100>, <111>, and <000>, together with the relative temperature coefficients, density of states, and relative mobilities. From these data, it was possible to determine that the <000>-<111> separation in E-k space is dependent on purity. Low temperature Hall measurements allowed the determination of the ionization energy as a function of alloy composition and purity. Optical absorption data showed that, β, the temperature coefficient of the band gap, is -4.5×10^{-4} ev/^{o}K for pure GaSb, as opposed to the value often quoted of -3.0×10^{-4} ev/^{o}K. β increases monotonically with increasing InSb constant to about -3.75×10^{-4} ev/^{o}K at 8 mol.% InSb. No discontinuities in the relation between β and alloy composition for the p-type specimens studied were found.

4.2 Characterization of InSb by X-Ray Anomalous Transmission

The growth characteristics of indium antimonide have been studied using high resolution chemical etching techniques, and by x-ray anomalous transmission topography and rocking curve analysis. A layer type growth model was found to be consistent with both the etching and x-ray topographical analysis, on the core and off-core crystal melt interfaces. Impurity induced strain was found in all doped crystals. The configurations indicated further, the presence of macroscopic dopant heterogeneities not revealed by etching techniques. The configuration of the macroscopic strain patterns was shown to be a function of growth conditions. An atomic growth model consistent with the observed directionality of the strain, or lattice bending was developed. Rocking curve measurements showed large variations of $K\alpha_1 - K\alpha_2$ spacing corresponding to d-spacing of up to 10 percent at the "A" and "B" surfaces of perfect indium antimonide crystals. Differences of equal magnitude were observed on different areas of surfaces of crystals containing dopant heterogeneities and other defects. The d-spacing variations were related to crystalline polarity and dopant induced

lattice strain, respectively. A perfection parameter $\rho = \exp(\mu^{\circ}_{eff} - \mu_{eff})$ was introduced (μ°_{eff} and μ_{eff} are the effective absorption coefficients of a perfect and a real crystal, respectively). This parameter proved to be a meaningful indicator of total crystalline perfection, since the anomalously diffracted x-ray beam is inherently sensitive to dislocation density as well as to any other deviation of the lattice from perfection. Integrated intensity measurements of the core and off-core regions have indicated that the off-core region is less perfect than the core region despite similar dislocation densities. A ratio of the perfection coefficient of the core and off-core regions was measured to be 1.2 for 5×10^{18}/cc tellurium.

4.3 Impurity Heterogeneities in Germanium

Impurity heterogeneities (striations and impurity cores) were systematically revealed for the first time in germanium grown from the melt by the Czochralski technique, using high resolution etching and interference contrast microscopy techniques. The distribution of impurities was studied under all possible combinations of seed and crucible rotation during growth, and was related to the thermal asymmetry present in the furnace. Excellent homogenization of impurity distribution was achieved under a sufficiently high rate of crucible rotation alone, thereby suppressing effects of thermal convection, minimizing impurity accumulation at the growth interface, and avoiding adverse effects of thermal asymmetry by not employing seed rotation. Four-point-probe resistivity profiles at room temperature revealed for the first time that the average impurity concentration of homogeneous regions was significantly lower than that of striated regions. This result confirms the conclusion that the average "true" crystal growth rate in the presence of rotational remelting must exceed the average pulling rate, and increase the average impurity distribution coefficient at the growth interface. Systematic increases in Hall mobility were found for homogeneous material versus striated material in all crystals investigated, the increase exceeding 20 percent for medium concentrations of impurity. These results were found to be consistent with a physical model whereby mobility is affected at high concentrations by an electric field distortion effect only, while at medium and low concentrations it is primarily limited by an additional scattering mechanism (as evidenced by different temperature dependences). Such scattering is the result of the striated impurities forming space charge regions that rapidly grow in extent with decreasing concentration.

4.4 Growth and Characterization of Silicon

In the first phase of this investigation we developed surface preparation and high resolution etching techniques suitable for the study of dopant heterogeneities in silicon. Best results were obtained by chemical-mechanical polishing and the use of a CrO_3-HF-H_2O etchant. This treatment results in a linear resolution for dopant heterogeneities of better than 2μ in both n-type and p-type material of about 10 m.. resistivity. The etching experiments revealed that the linear resolution (contrary to Ge and InSb) is independent of the orientation of the exposed plane. The growth experiments were performed in an R.F. heated Czochralski-type pulling system which had been modified to permit Peltier-pulsing during growth. High resolution etching of Sb (n-type) and Ga (p-type) doped single crystals revealed coring and extensive dopant heterogeneities in the form of striations. These heterogeneities could be attributed to magnetohydro dynamic effects associated with R.F. heating. At present the resolution of the etching process is insufficient to permit unambiguous differentiation between Peltier striations and otherwise induced dopant heterogeneities. This investigation is part of an effort to develop a growth system capable of pulling single crystals under zero gravity conditions in outer space. Because of the absence of wetting between the charge (Si-melt) and the crucible liner (SiO_2) it is necessary to design appropriate orifices (covering the melt surface) through which single crystals of silicon may be pulled. This problem is currently under investigation.

4.5 Czochralski Growth in Transverse Magnetic Fields

A Czochralski type crystal puller used in previous studies was adapted to a 4" pole gap electromagnet for growth experiments in transverse magnetic fields of up to 4000 gauss. Upon applying a magnetic field (1000 gauss) the temperature of the melt (InSb in contact with a seed and at thermal steady state) increased by several degrees. This temperature increase is attributed to an increase in the "effective" viscosity of the melt which leads to diminished thermal convection and thus to decreased heat-losses. At the same time the thermal asymmetry in the system (manifested during rotation as a periodic temperature fluctuation) was observed to become more complex. The "increased" viscosity apparently decreased convection so that inherent irregularities in horizontal thermal gradients were preserved during rotation. This was confirmed by measurements with rotating thermocouples and the thermal irregularities attributed to non-uniform heat inputs

and heat losses. The effect of the applied magnetic field on the thermal configuration of the system was unambiguously reflected in the dopant distribution of the growing single crystals of InSb. In the part of the crystal grown without an applied magnetic field the usual rotational striations are clearly present. The increase in temperature upon turning on the magnetic field is reflected in extensive remelting of the previously equilibrated seed. Until steady state thermal conditions are established the spacing of the rotational striations is found to (at constant pulling rate) increase gradually. At steady state these striations exhibit complex substructures reflecting the irregular thermal conditions "frozen in" by the magnetic field. The effects of transverse magnetic fields on growth characteristics in the absence of seed rotation are minor as long as only moderate thermal gradients are applied to the melt.

4.6 Thermal Effects on Crystal Pulling

Investigations of the growth characteristics of InSb by means of rate striations revealed that the dopant incorporation and distribution in off-core regions is primarily controlled by the microscopic instantaneous growth rate. Random fluctuations of boundary layer thickness or dopant concentration fluctuations in the accumulation layer (caused by thermal convection) are negligible and do not affect the dopant incorporation. Attempts to establish "perfect" thermal symmetry in a special Czochralski pulling system equipped with x-y-z adjustment capability of the circular heating element failed. A residual asymmetry component was found to be caused by non-symmetric heat losses due to the presence of windows and other unavoidable auxilary equipment in the growth system.

A study of the growth characteristics of Ge in the same system showed contrary to InSb (melting point 525^{o}C) that at the required higher temperature for germanium pulling (melting point 948 ^{o}) the impurity incorporation and distribution is greatly affected by increased thermal convection and pronounced compositional fluctuations can be observed in the off-core region at constant microscopic growth rates.

5.0 Decomposition of Silver (II) Oxide

Personnel: H. C. Gatos, A. F. Witt, O. A. Sandven

Sponsorship: NASA

The isothermal decomposition of silver (2) oxide $4AgO \rightarrow 2Ag_2O + O_2$ was studied in the temperature range from 111°C to 133°C by means of decomposition weight loss and the associated change in electrical resistivity. The experiments were performed in a dynamic system, with an ambient atmosphere of air or argon at various pressures, using both cold pressed specimens and powder samples. At 1 atm pressure, the decomposition was found to occur predominantly by rapid surface nucleation of the product phase (Ag_2O), followed by three-dimensional growth of these nuclei. In the initial stage, the radial rate of growth is proportional to $t^{1/3}$, resulting in a constant rate of decomposition. In the intermediate stage, the radial rate of growth of the Ag_2O-grains is constant and the decomposition rate increases. After the decomposed fraction α reaches a value of about 0.5, the Ag_2O product phase grains start to overlap, and the decomposition rate decreases. The final stage of decomposition takes place by monomolecular decay. Large specific surface area of the reactant phase, or introduction of plastic deformation, results in higher decomposition rates because of increased surface nucleation. The activation energies for the decomposition process were found to be 24 kcal/mole for the initial stage, 31 kcal/mole for the intermediate stage and 16 kcal/mole for the final stage. In vacuum (10^{-6} torr) decomposition takes place mainly by bulk nucleation. The process is a 1st order reaction, except in the initial stage where surface nucleation and growth causes a deviation from 1st order behavior. The activation energy for the initial stage was found to be 20 kcal/mole. For the main portion of the reaction, (1st order reaction) the activation energy is 40 kcal/mole. The rate of reaction is higher than at 1 atm ambient pressure, and the desorption of the gaseous reaction products appears to be the rate determining process under these conditions. Electronic conduction in cold pressed samples of AgO was found to take place predominantly in the surface region of the individual grains. During decomposition at 1 atm, the resistivity increases rapidly due to retardation of the growth of these grains by overlap with secondary nuclei. The activation energies for the resistivity increase are in good agreement with the activation energies for decomposition under all conditions.

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N. S. Platakis, "Semiconducting Properties of the System $(1-x)As_2Se_3.xSb_2Se_3$ In Its Amorphous and Crystalline State", Ph. D. Thesis, Department of Metallurgy and Materials Science, June 1970.

J. M. Sandor, "Impurity Heterogeneities and Associated Electrical Characteristics of Germanium Single Crystals", Ph. D. Thesis, Department of Metallurgy and Materials Science, September 1970.

O. A. Sandven, "Isothermal Decomposition of Silver (2) Oxide", Sc. D. Thesis, Department of Metallurgy and Materials Science, June 1970.

R. Singh, "Impurity Distribution in Single Crystals Pulled from the Melt-Interface Instability in Czochralski Grown Gallium Doped Germanium Single Crystals", Sc. D. Thesis, Department of Metallurgy and Materials Science, June 1970.

D. C. Miller, "The Growth Characteristics of Indium Antimonide as Revealed by Chemical Etching and X-Ray Anomalous Transmission", Ph. D. Thesis, Department of Metallurgy and Materials Science, September 1970.

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M. Lichtensteiger, I. Lagnado and H. C. Gatos, "P-Type Cadmium Sulfide Crystalline Films", Appl. Phys. Letters, 15, 418 (1969).

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Sponsorship:
*Advanced Research Projects Agency, SD-90, DSR 75134 and DSR 72224
National Science Foundation, GK-2911, DSR 71029
Office of Naval Research, Nonr 3963-16, DSR 74611 and

Research Report

1.0 High-Field High Temperature Superconductivity: Structure and Properties

1.1 Severely Deformed Nb-Ti Alloys (Rose, Puffer, Kohr; ARPA)

Severely deformed Nb-40%Ti and Nb-60%Ti wires were fabricated from annealed rods by composite techniques in order to determine whether critical field enhancement did occur in a manner similar to the case of Nb (see Section 2.1). An increase of at least 15% was noted on the first try, which was attended with difficulties due to limited ductility. It was concluded that higher enhancements were possible given proper heat treatments and drawing and swaging temperatures, and that the effects were similar to those in pure Nb. Practical use of such techniques in high-field magnet materials will probably be limited due to other fabrication problems, e.g. the presence of the Cu (or other) stabilizing matrix.

1.2 Superconductivity of Nb_3Al (Rose, Kohr, Petrovich; NSF)

For various reasons the compound Nb_3Al appears at this time to be the best prospect for practical use as a high temperature high field superconductor. The problems which impede the use of this material appear to be metallurgical in nature. We have initiated a systematic search for the optimal means of producing this compound, the critical structural features responsible for the wide variation in its properties, and the relation of such structure to processing.

2.0 Superconductivity in the Transition Metals

2.1 The Critical Field of Severely Deformed Nb (Rose, Hill; NSF)

The model previously proposed, that the anomalous magnitude and anisotropy of the resistive critical field of severely deformed Nb is due to superconductivity in the cell walls, was tested in several ways. First, we

observed that since the cell size decreases with deformation, it should be possible to wipe out all or most of the anomalies if sufficient deformation could be introduced to reduce the cell size to the order of the range of coherency. We succeeded in the latter and the anticipated shrinkage of magnitude and anisotropy of the critical field did indeed occur. Second, we observed that the same effect could be achieved if, instead of decreasing cell size, the range of coherency was increased. The latter was achieved by raising the temperature to the vicinity of T_c, and in fact it was possible to calculate the cell size as a function of deformation from the temperatures at which the anisotropy disappeared. The effect of uniaxial stress, both tensile and compressive, was also measured as a function of strain. It was found that the stress sensitivity of the resistive critical field increased greatly with deformation to more than an order of magnitude higher than the accepted bulk value, and was almost even-valued, whereas the true bulk property is thermodynamically required to be odd-valued. This behavior, together with all of the other observations, can be explained by the existence of doubly-locked dislocation pileups which act as stress multipliers. Still another test was applied by measuring the spread of the resistive transition as a function of strain, revealing that the local stress rather than the RMS stress in the cell wall was the important parameter. Since this conclusion implies the existence of small superconducting regions in the cell wall even at very high fields, measurements were made at the National Magnet Laboratory and transitions were found to occur at low current densities at applied fields up to 48 KG.

2.2 Is Vanadium Allotropic? (Rose, Lewis; NSF)

Seemingly anomalous behavior of vanadium abounds in the literature, with over fifty papers describing a transformation occurring at either 180°K or 240°K or thereabouts. There is little agreement as to why the disparity in temperature occurs or the nature of the transformation itself. We have done a series of resistometric and x-ray measurements on specimens of varying purity, ranging from commercial stock to single crystals grown in ultra-high vacua. One fact has been confirmed: there are in fact two transformations, not one, and they occur at 180°K and 240°K, approximately. We have tentative evidence that the 240°K transformation is second-order and the 180°K transformation is a genuine structural change. To confirm the latter we are proceeding with x-ray work.

2.3 Controlled Pinning by Surface Microgrooving (Rose, Morrison; NSF)

We have created pinning centers of known strength and spacing by

pressing diffraction gratings into the surfaces of In-Bi or Pb-Tl foils which have been cast under rigidly controlled conditions. The spacing of the grooves is thereby well-known and also eliminates the necessity of calibration when the groove width is determined by the scanning electron microscope. From the blaze angle of the grating the groove depth and geometry are readily known. We have shown that such grooves effectively control flux flow, have derived quantitative formulae for the dynamic and static pinning forces and resolved many questions posed by other investigators, e.g. the role of surface pinning and also the $J_c(H)$ peak.

3.0 Tunneling

3.1 Synthetic Tunnel Barriers (MacVicar, Frommer; ONR)

We have been able to get reasonable tunneling data from a number of materials using thin evaporated carbon barriers.

3.2 The Energy Gap of Rhenium Single Crystals (Rose, MacVicar, Puffer, Ochiai ONR)

We have measured the anisotropic energy gap of rhenium as a function of orientation, using carbon films as barriers on the surfaces of rhenium single crystals. The carbon films were used because the oxides of rhenium conduct electricity too well. The anisotropy of the gap in rhenium appears to be related to the phonon spectrum rather than the Fermi surface.

4.0 Radio Frequency Superconductivity

4.1 Superconducting Resonant Circuits (Rose, Puffer, Sheung, Weinman; ARPA)

Apparatus has been constructed to measure quality factors of circuits with resonant frequencies from 50 to 1000 MHZ. Trial runs on crude high purity lead helical resonators showed $Q \sim 4 \times 10^5$ with no annealing or other treatments.

4.2 RF Losses and Fluxon Pinning (Rose Puffer, Yasaitis, Weinman; ARPA)

Superconductors exhibit characteristic steep rises in RF resistivity which have been ascribed to pinning. We are testing this explanation by using foils with controlled pinning, prepared by the techniques mentioned in Section 2.3. Apparatus for measurement of RF resistivity below 50 MHZ has been constructed.

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In Press:

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S. I. Ochiai, M. L. A. MacVicar and R. M. Rose, "Tunneling into a Superconducting Rhenium Single Crystal," to appear in Solid State Commun.

VII POLYMERS AND GLASSES

Faculty:

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Graduate Students:

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M. Cukierman, Fairchild Camera and Instrument Fellow
R. W. Hopper, American Optical Fellow
C. Lee, Olin-Mathieson Trainee
* A. Pierre, Research Assistant
A. W. Schneider, National Science Foundation Trainee
M. Tsai, Owens-Illinois Fellow

Sponsorship:

* Advanced Research Projects Agency, SD-90, DSR 75127, 72227
American Optical Company
Fairchild Camera and Instrument Corporation
National Science Foundation
Owens-Illinois Inc.

Research Report

1.0 Inclusion Damage in Laser Glass

Personnel: Professor D. R. Uhlmann; R. W. Hopper; C. Lee

Sponsorship: Advanced Research Projects Agency; American Optical

The mechanism of inclusion damage in laser glass has been associated with the temperature rise of particle, or surface regions of particles, relative to the surrounding glass. The particles of greatest concern are metallic, although at very high power levels ceramic inclusions containing large concentrations of high-absorbing ions can likewise result in failure.

Solutions to the heat flow problems of a perfectly conducting sphere in a medium of finite conductivity and of the infinite composite solid indicate that temperatures of metal particles subject to a 20 j cm^{-2}, 30 ns laser pulse can exceed 10,000^{o}K for a range of particle sizes. These high temperatures produce stresses in the glass adjacent to the particle which can exceed the theoretical strength of the glass, and result in failure.

The effects on the breakdown condition of flux level and pulse time, as well as the size, shape, thermal expansivity, and spectral emissivity of the particle, and the heat capacity and thermal conductivity of particle and glass have been specified. Observations of damage morphologies have been carried out and related to the results of the calculations. A fatigue phenomenon is anticipated under certain conditions, and the phenomenon of phase separation is not expected to affect significantly the process of inclusion damage. Likely sources of metallic inclusion particles in laser glasses have been considered, and melting conditions most suitable for their avoidance have been suggested.

2.0 Viscous Flow and Relaxation Phenomena

Personnel: Professor D. R. Uhlmann

Sponsorship: Advanced Research Projects Agency

Studies of viscous flow and volume relaxation are being carried out to elucidate the characteristics of these phenomena in various systems. Attention is being directed to a number of relatively simple organic liquids, as well as to several inorganic liquids. In all cases, the materials selected for study form amorphous solids when cooled at reasonable rates from the liquid state.

The view is being advanced that free volume models can provide a useful description of the flow process at relatively elevated temperatures (relative low viscosities), but that such models are inadequate for describing flow in the high viscosity region around the glass transition. At high viscosities - higher than perhaps 10^5 - 10^7 poise - an easier process than that implied by the free volume approach seems to be operative; and this faster process may well be best described in terms of a potential energy model.

3.0 Theory of Diffuse Interfaces

Personnel: Professor D. R. Uhlmann; R. W. Hopper

Sponsorship: Advanced Research Projects Agency; American Optical Co.

The theory of diffuse interfaces has been extended to treat finite systems containing more than a single interface. The variation of the surface energy with separation between the interfaces has been considered from the viewpoint of a pair interaction model as well as a standard form of diffuse interface theory. Both approaches indicate that the surface energy is a monotonically decreasing function of separation for a clustering solution. Also being considered are the effects of various higher order terms on the expected kinetics of spinodal decomposition.

4.0 Particle Coalescence and Phase Separation

Personnel: Professor D. R. Uhlmann; R. W. Hopper

Sponsorship: Advanced Research Projects Agency; American Optical Co.

The mechanism by which interconnected submicrostructures develop in many glasses is of considerable interest. The technological interest is enhanced by the difficulty of distinguishing unequivocally between two alternative mechanisms: spinodal decomposition, and nucleation and growth followed by particle coalescence (NGC). While particle coalescence has been observed in at least one system, there has been a strong theoretical objection to the NGC model - viz. that two spheres growing by a diffusion-controlled process from a matrix phase will not grow together in a finite time because of interparticle interference effects.

Attention is therefore being directed to various mechanisms whereby coalescence might occur despite such interference effects. The mechanisms analyzed to date include heterogeneous nucleation of a neck joining the two particles, volume diffusion driven by capillarity, and diffusion driven by a variation of surface energy with interface separation. In all cases, the results indicate that coalescence can take place in reasonable times and that NGC should be viewed as a reasonable alternative to spinodal decomposition as a mechanism for producing interconnected structures in glasses.

5.0 Small Angle X-Ray Scattering Studies of Glasses

Personnel: Professor D. R. Uhlmann; A. Pierre; F. N. Molea (Harvard University); Dr. T. P. Seward (Corning Glass Works); Dr. R. R. Shaw (American Optical Co.)

Sponsorship: Advanced Research Projects Agency; Corning Glass Works, American Optical Co.

Small angle x-ray scattering can be a powerful tool for investigating heterogeneities in glasses. Such studies are presently being carried out to elucidate structural characteristics in two types of glasses: (1) single-component materials and apparently - homogeneous multi-component materilas; and (2) materials which exhibit the phenomenon of phase separation. In the former area, the glasses presently being investigated include GeO_2, SiO_2 and some alkali silicates; while in the latter area, attention is being directed to ternary glasses based on the binary systems BaO - SiO_2 and PbO-SiO_2.

6.0 Phase Separation and Properties of Glasses

Personnel: Professor D. R. Uhlmann; Dr. R. R. Shaw (American Optical Co.)

Sponsorship: Advanced Research Agency; American Optical Co.

The effects of phase separation on the properties of glasses are being

considered. Initial attention is being directed to simple binary glass systems. The effect on density has been analyzed in terms of a simple model which assumes volume additivity of the two phases. The results have been used to describe property variations in systems where miscibility gaps have been determined, as well as to predict immiscibility behavior in systems where such information is lacking.

The effects of phase separation on elastic moduli have been described in terms of standard models for the elastic properties of two-phase materials. The Hashin-Shtrickman lower bound and the equivalent Kerner relation were found to provide the best description of the elastic properties over the complete range of second-phase volume fraction. The predictions of immiscibility behavior based on consideration of elastic moduli variations are in consonance with those based on consideration of density relations.

7.0 Crystallization and Melting in Glass-Forming Systems

Personnel: Professor D. R. Uhlmann, M. Tsai

Sponsorship: Advanced Research Projects Agency; Owens-Illinois, Inc.

Studies of crystallization and melting in glass-forming systems can provide important information for elucidating the general nature of crystal growth from the melt. Studies carried out to date have indicated that for materials with large entropies of fusion ($\Delta S_f > 4R$), the crystal-liquid interface is faceted under all conditions of growth and non-faceted in melting; the interface site factor increases with increasing undercooling; and marked anisotropy is observed in the rates of crystallization and melting in the vicinity of the melting point. In contrast, for materials with small entropies of fusion ($\Delta S_f < 2R$), the interface morphologies are observed to be non-faceted under all conditions of growth and melting, the interface site factor is independent of undercooling or superheat, and the curves of melting rate and crystallization rate are continuous with the same slope through the melting point.

Presently being investigated are the effects of impurities on the kinetics of crystallization and melting and on the interface morphologies. The initial studies have been concerned with glasses in the Na_2O-GeO_2 system; and results obtained to date indicate a pronounced effect of even small Na_2O additions (in the range of 0.1%) on the kinetics of crystallization. These kinetic effects will be compared with the effect of Na_2O additions on the melt viscosity, and specific attention is being directed to the expected transition from inter-face-controlled growth to diffusion controlled growth.

8.0 Structure of Glasses

Personnel: Professor D. R. Uhlmann; M. Cukierman; Professor B. E. Warren, Department of Physics (ret.)

Sponsorship: Advanced Research Projects Agency; Fairchild Camera and Instrument Corporation.

Recent advances in experimental techniques and means of analyzing data appear to have opened a new era of diffraction studies of glass. These advances permit more definitive conclusions to be drawn concerning the structure of individual glasses.

These techniques are now being applied in diffraction studies of a number of simple glasses. The principal thrust of these studies is a determination of the structural state of the common modifying cations in glasses, the effect of cation additions on the framework structure, and the relation between the structural characteristics and various properties of the glasses.

Experimental results, obtained in the region of large $\sin \theta / \lambda$ with the rhodium tube - molybdenum foil technique of Warren, are in hand on GeO_2 and a number of alkali silicates and alkali borates; and work is being undertaken on other alkali silicates as well as glasses in the Na_2O-GeO_2 system. The data already obtained is in the course of analysis.

9.0 Deformation of Amorphous and Semi-Crystalline Polymers

Personnel: Professor D. R. Uhlmann

Sponsorship: Advanced Research Projects Agency

The deformation of amorphous and semicrystalline polymers is being investigated. Emphasis is being placed on the relation between the mechanical properties and various structural and microstructural characteristics of the materials. Particular concern is being directed to various crystallization and orientation parameters, and their relation to the deformation process. The polymers presently being investigated include polyethylene, polypropylene, nylon, polycrabonate, and polystyrene.

10.0 Crystallization of Polymers Under Pressure

Personnel: Professor D. R. Uhlmann; P. D. Calvert

Sponsorship: Advanced Research Projects Agency

The crystallization of a number of polymers under high pressure has been shown to result in an extended-chain crystalline conformation, in contrast with the usual folded-chain conformation commonly observed in atmospheric pressure crystallization. The origin of this extended-chain morphology is presently being investigated, as is its effect on mechanical properties. Initial studies of the crystallization behavior of polyethylene at high pres-

sure have indicated that the growth of extended-chain crystals can take place quite rapidly at high pressure, and that the extended-chain crystals produced by high pressure treatment can reflect a crystallization morphology and not merely represent a large-scale annealing of folded-chain cyrstals.

Consideration is presently being given to crystallization of other polymers at high pressure and to the relation between the crystallization behavior and various structural characteristics of the polymers.

11.0 Crystallization of Polymers

Personnel: Professor D. R. Uhlmann; P. D. Calvert

Sponsorship: Advanced Research Projects Agency

The effect of crystallization conditions on the morphology of semi-crystalline polymers is being investigated, with initial attention being directed to polyethylene and polypropylene. Also being considered is the effect on crystallization behavior of the structure of the polymers.

Theoretical work is being carried out on the general problem of polymer crystallization. Model calculations carried out to date raise questions concerning our knowledge of the structure of semi-crystalline polymers, and suggest that it may be misleading to generalize from results obtained on solution-grown crystals to describe crystallization from the melt.

12.0 Characteristics of Anomalous Water

Personnel: Professor D. R. Uhlmann; Professor D. Turnbull (Harvard Univ.); C. Lee; A. W. Schneider

Sponsorship: Advanced Research Projects Agency; National Science Foundation; Owen-Mathieson Chemical Company

A new form of water, known as anomalous water or polywater, has been reported by a sizable number of investigators both here and abroad. This form of water, which was originally prepared by condensing at slight undersaturations in glass capillary tubes, can have unusual properties, including a boiling point as high as 200°C, a density as high as about 1.3, and a glass transition temperature about - 40°C.

Objections have recently been raised to the view of anomalous water as a new form of water, and a number of investigators have associated the anomalous properties with various impurities. Work in our group has demonstrated that materials having the important characteristics of anomalous water - designated apparently anomalous water (AAW) - can be produced by the exposure of a number of oxide materials to water. The materials on which AAW has been found include borosilicate glass, fused silica, silica sand and borax. The infrared and Raman spectra, as well as the freezing point depression, can be

related to the impurities indicated by chemical analysis. The impurity present in largest concentration in the present work was generally S, although significant concentrations of Na, Cl, B were found as well in some cases (depending on the preparation conditions).

This work has led to a simple method for producing AAW in sizable quantities - viz., exposure of some standard silica gels to the laboratory atmosphere, followed by heating the gel to elevated temperatures to drive off the water, collecting the water and concentrating it to the desired extent.

Problems of characterizing the state of the impurities in AAW and their effect on the measured properties are presently being investigated. Also being carried out are studies of AAW produced in other ways, including condensation in capillaries and on plates, on a variety of substrates.

Publications

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R. W. Hopper and D. R. Uhlmann: "On the Mechanism of Inclusion Damage in Laser Glass", Accepted for publication, J. Appl. Phys.

R. W. Hopper, C. Lee and D. R. Uhlmann: "The Inclusion Problem in Laser Glass", to appear in Proceeding of Second Symposium on Damage in Laser Materials, National Bureau of Standards, Washington, D. C.

R. R. Shaw and D. R. Uhlmann: "Effect of Phase Separation on the Properties of Simple Glasses. I. Elastic Properties", accepted for publication, J. Non-Cryst. Solids.

J. B. Park and D. R. Uhlmann: "Recovery of Deformed Polymers. I. Retraction of Cold-Drawn Polycarbonate, Polyethylene and Polypropylene", accepted for publication, J. Appl. Phys.

R. M. Kimmel and D. R. Uhlmann: "Effects of High Pressure on Amorphous Polymers: Densification of Polymethlyl Methacrylate", accepted for publication, J. Appl. Phys.

VIII. METALS PROCESSING - CASTING AND SOLIDIFICATION

(All personnel from Department of Metallurgy and Materials Science)

Faculty:

* M. C. Flemings, Professor

Research Staff:

T. Z. Kattamis, Research Associate
R. Mehrabian, Research Associate
* E. H. Backman, Foreman
R. G. Riek, Research Staff Member

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L. K. Bigelow, Research Assistant
T. W. Caldwell, Teaching Assistant
A. J. Campagna, Research Assistant
D. S. Gnanamuthu, Research Assistant
P. A. Joly, Research Assistant
M. A. Keane, Research Assistant
S. A. Metz, Research Assistant
M. Myers, Research Assistant
E. S. Palmer, Teaching Assistant
M. D. Rinaldi, Teaching Assistant
A. M. Reti, Research Assistant
F. M. Schlecht, Graduate Student
D. R. Spencer, Research Assistant
L. R. Stumbar, Teaching Assistant
J. C. Yarwood, Research Assistant

Support Staff:

* J. F. Stack, Technician
A. J. Zona, Engineering Assistant
A. Barbara Rich, Secretary

Degrees Granted:

L. K. Bigelow, Sc.D., Metallurgy, February, 1970

A. J. Campagna, Ph.D., Metallurgy, July, 1970

S. A. Metz, Ph.D., Metallurgy, June, 1970

M. Myers, Sc.D., Metallurgy, July, 1970

A. M. Reti, Sc.D., Metallurgy, June 1970

F. M. Schlecht, S.M., Metallurgy, July 1970

Sponsorship:

Army Materials Research Agency, DAAG-46-68-C-0043, DSR 70811

Army Materiel Command, DAAG-25-69-C-0489, DSR 71454

Office of Naval Research, NONR-3963(09), DSR 79988

American Foundrymen's Society, DSR 70438

Advanced Research Projects Agency, DSR 78893

American Iron and Steel Institute, DSR 70544

American Iron and Steel Institute, DSR 71119

Advanced Research Projects Agency, DSR72542

Army Research Office-Durham, 72610

Research Report:

Research is primarily concerned with liquid-solid transformations; a central aim of the research is to gain greater control over structure and properties of materials through control of solidification. Work is currently under way in the following areas:

1.0 Crystal Growth (ARPA)

Personnel: J. F. Stack, E. H. Backman, R. Mehrabian

Continuing progress has been made in establishment of the Metal Crystal Growth Facility as part of the Center for Materials Science and Engineering. Research on crystal growth has included continuation of study of growth of "composite" crystals and study of crystals grown under conditions of extremely vigorous fluid flow.

2.0 Effect of Fluid Flow on Structure; Composite Materials (ONR)

Personnel: M. D. Rinaldi, D. R. Spencer

Current work is on solidification with a "composite" eutectic-like structure of aluminum alloys that are far from eutectic composition. Work is on binary aluminum-copper alloys and on ternary aluminum-copper-nickel alloys.

Other work on convection includes continuation of a study of effects of extremely vigorous convection on solidification structure. Apparatus is being employed which is designed to achieve velocity gradients at a solidifying liquid-solid interface the order of 10^5/sec. These gradients are far in excess of those obtained in any previous solidification study. Experiments show significant influences of the flow on structure.

3.0 Macrosegregation (AISI, ONR)

Personnel: R. Mehrabian, M. A. Keane

This research comprises analytical and experimental study of macrosegregation in ingot solidification. Results of this research show that most, if not all, commercially important types of macrosegregation in castings and ingots result from a single basic cause. That cause is flow of solute-rich liquid between dendrites in the liquid-solid region of the partially solidified casting or ingot. Driving forces for the flow are solidification contraction, thermal contractions of liquid and solid, and gravity acting on fluid of variable density.

4.0 Inclusions (Army, AISI)

Personnel: T. Z. Kattamis, L. K. Bigelow, M. Myers, D. L. Baty, D. S. Gnanamuthu, M. Basaran

Several related activities are under way, designed to study the formation and growth of non-metallic inclusions in metal melts (especially in steel). Inclusion nucleation and growth is being studied in a number of ternary iron base alloys including Fe-S-O, Fe-Si-O, Fe-Mn-S, and low alloy steel. Inclusion "pushing", coalescence, and ripening are being studied. Effects are being examined of high temperature homogenization treatments on morphology of inclusions in cast steel. Also being studied is influence of inclusion morphology and chemistry on mechanical properties.

5.0 Ultra-High Strength Aluminum Alloys (Army)

Personnel: A. J. Campagna, D. Apelian, T. W. Caldwell, E. S. Palmer

Influence of solidification heterogeneities on properties of wrought aluminum alloys is being studied in this program. It has been shown that by careful control of solidification and thermo-mechanical processing significant improvements in properties of wrought aluminum alloys can be obtained. Current emphasis of this work is on (1) refining the cast structure of aluminum ingots by special means of control of heat flow, (2) removal of oxide and other heterogeneities from the melt by filtration, and (3) behavior of "anti-recrystallizers" (Mn, Cr, Zr) during solidification

and subsequent thermo-mechanical processing.

6.0 Rheology of Partially Solidified Metal Alloys (ARO)

Personnel: D. R. Spencer, L. R. Stumbar

Work is being conducted on the deformation and flow behavior of partially solidified alloys. Initial work is on low melting point alloys. Flow properties are measured with specially constructed viscometers, and structure after deformation is studied in detail. One practical objective of this study is to examine conditions necessary to develop a process which would permit casting alloys in the "semi-solid" state.

7.0 Production of Wrought Material from Alloy Powders (ARPA)

Personnel: R. Mehrabian, L. R. Stumbar, R. G. Riek, A. J. Zona

This research is part of a larger program at M.I.T. designed to study feasibility of producing wrought material of highly alloyed iron and nickel-base alloys from specially produced powders. Our research is on methods of improving the solidification behavior of the finely divided alloys.

Theses:

L. K. Bigelow, "Sulfide Inclusions in Steel", Sc.D., Department of Metallurgy and Materials Science, February, 1970

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S. A. Metz, "Hot Tearing", Ph.D. Department of Metallurgy and Materials Science, June, 1970

M. Myers, "Behavior of Silica Inclusions During Solidification of Iron-Base Alloys", Sc.D. Department of Metallurgy and Materials Science, July, 1970

A. M. Reti, "Thermomechanical Processing of Aluminum Alloys", Sc.D., Department of Metallurgy and Materials Science, June, 1970

F. M. Schlecht, "Plane Front Solidification of Polyphase Ternary Alloys", S.M., July, 1970

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Accepted for Publication:

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M. C. Flemings, R. Mehrabian, "Unidirectional Solidification", Trans. AFS.

S. A. Metz, M. C. Flemings, "Hot Tearing", Trans. AFS.

M. C. Flemings, R. Mehrabian, "Segregation in Castings and Ingots", ASM.

IX X-RAY AND ELECTRON OPTICS LABORATORY

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Research Staff:

L. V. Sutfin, DDS, Post Doctoral Fellow, Nutrition and Food Science

Graduate Students:

J. S. Duerr, Research Assistant
W. K. Jones, Teaching Assistant
C. E. Lyman, Teaching Assistant

Support Staff:

J. A. Adario, Technician
J. I. Herman, Technician
Peggy Carney, Secretary

Sponsorship:

National Aeronauticas and Space Administration, NsG-496 (part), DSR-70479
National Institute of Dental Research, DE-105, DSR 71256
Smithsonian Astrophysical Observatory

Personnel who have left:

A. J. Saffir, DMD, Post Doctoral Fellow, Nutrition and Food Sci. (Now at Materials Analysis Corp., Palo Alto, Cal.)

Degrees Granted:

A. J. Saffir, Ph.D., Nutrition and Food Sci. Feb. 1970

Sponsorship:

NASA, NsG-496 (part), DSR-70479
National Institute of Dental Research, DE-105, DSR 71256
Smithsonian Astrophysical Observatory

Research Report:

Study of Metallic Meteorites

Personnel: J. S. Duerr

Sponsorship: Smithsonian Astrophysical Observatory

Research has continued in an effort to more fully define the thermal-mechanical history of metallic meteorites. The specific goal in the present work is to determine the role of each of several possible phase transformations in the formation of plessite and the temperatures at which such transformations occur for the composition and cooling rates representative of metallic meteorites. A number of meteorites have been selected from the different classifications based on bulk nickel content, Ga-Ge content, and cooling rate. The plessite areas in each sample are being analyzed with the electron microanalyzer to determine nickel and carbon concentration profiles. For this study an automated stepping system was constructed for the electron microanalyzer to facilitate the carbon analysis. The sample is automatically traversed a set distance, a delay period is introduced to allow removal of surface carbon contamination, and the nickel and carbon X-ray intensities are recorded by typewriter.

Non-Dispersive X-ray Analysis With the Scanning Electron Microscope

Personnel: L. V. Sutfin

Sponsorship: National Institute of Dental Research; Office of Naval Research

The aim of this work is to improve on the spatial resolutions that are obtainable with the conventional electron microanalyzer.

Techniques for improving the efficiency of X-ray detection are being developed for use in analysis in which volumes with sub-micron dimensions are of interest. This is necessary if elemental distributions within cells and the nature of intracellular organelles are to be studied. The scanning electron microscope will be utilized for visualization and excitation of the sample. Non-dispersive analysis of X-ray spectra is being employed. Emphasis is being placed on light element detection.

Both a lithium drifted silicon detector and a gas flow proportional counter are being used to detect X-ray signals gen-

erated. The detection covers Be Kα through the maximum energy excited by the 20 KV beam. Energy resolution ranges from 180 ev for Be Kα to 620 ev for photons with energies near 20 KeV. The output is displayed on a 1024 channel analyzer with spectrum stripping and intergration capabilities. Plotted, printed and punched paper tape outputs are available.

The system is applicable to any material and analyses of phases in dental amalgam have been performed.

It should be possible to analyze microtome sections of biological material with a resolution of 1000Å. This would be one order of magnitude better than that done in conventional probe analysis.

Electron Energy Analysis in Electron Microscopy

Personnel: C. E. Lyman

Sponsorship: Metallurgy Department

An electron energy analyzer is being built for installation in a commercial 100 KV electron microscope. This analyzer can image electrons which have lost various amounts of energy upon passing through a thin specimen. To disperse the electron beam a triangular magnetic prism is incorporated between the objective and intermediate lenses of the microscope.

In the conventional microscope both elastically scattered and inelastically scattered electrons go through the objective aperature and contribute to the image. If the inelastically scattered electrons are removed, chromatic aberration is minimized and the contrast is improved. This decrease in chromatic aberration would be helpful in the analysis of biological specimens and would also aid in the imaging of lattice planes.

An image may also be formed solely by electrons with the plasma energy loss characteristic of a certain element of compound; the brightness of the image being dependent upon the concentration of the element or compound. High resolution microanalysis on the order of 100 Å can be performed with this technique.

Dynamic Studies at Temperature on the Scanning Electron Microscope

Personnel: W. K. Jones

Sponsorship: Metallurgy Department

Because of the large depth of field and high resolution the S.E.M. is being utilized to study dynamic kinetic reactions. A hot stage, capable of 1000°C, has been constructed and coupled with a visual recording system, allows kinetic reactions to be studied as they occur.

Sintering of metallic microspheres, as an example, can occur by four possible mechanisms: evaporation-condensation, surface diffusion, viscous flow, and bulk diffusion. Research in the field has primarily been concerned with determining the primary mechanism for the material studied. Using the dynamic approach and the high magnification which can be obtained with the scanning electron microscope, we hope to obtain a better understanding of the rate controlling mechanism during the various stages of sintering.

Besides sintering, other topics of interest include phase transformations and high diffusivity mechanisms. Pearlite transformation, in both hypo and hypereutectic steels, is currently being investigated.

Publications:

L. V. Sutfin, and R. E. Ogilvie, "A Comparison of X-ray Analysis Techniques Available for Scanning Electron Microscopes," Proceedings of 3rd Annual Scanning Electron Microscope Symposium, April 1970.

L. V. Sutfin, R. E. Ogilvie and R. S. Harris, "Fracture of Dental Amalgam, A Scanning Electron Microscope Study," Journal of Dental Research, July-August Issue.

I PLASTIC DEFORMATION AND STRAIN HARDENING

Faculty:

A. S. Argon, Professor, Mechanical Engineering

Research Staff:

*H. Gleiter, Research Associate, Mechanical Engineering

Graduate Students:

G. H. East, Research Assistant, Mechanical Engineering

W. Wu, Research Assistant, Mechanical Engineering

Support Staff:

W. Henry, Instrument Maker, Mechanical Engineering

R. Graudins, Secretary, Mechanical Engineering

Sponsorship:

National Science Foundation Grant GK-3700, DSR 71350

* Advanced Research Projects Agency, SD-90, DSR 75109

Research Report

1.0 Easy Glide in Copper

Copper single crystals with dislocation densities of 10^3 cm^{-2}, prepared by prolonged annealing in an oscillating gradient furnace, and having yield stresses of 20 g/mm^2 were used to study multiplication of primary and secondary dislocations and the rate mechanism. It was found that the statistical accumulation of primary dislocations is in three distinctly different multipolar configurations: kink type walls normal to primary plane, streamers parallel to the primary plane, and irregular clusters. Increasing strain makes the kink walls more distinct, and straight, while the other multipoles grow without marked change in shape. The average spacing between kink walls decreases proportional to the square root of the flow stress which is consistent with their expected short range dipole layer stress field.

Secondary dislocations which act as forest to the primary plane increase in density proportional to the square of the flow stress indicating that they are not effectively paired. The rate of multiplication of the forest dislocations with change in axis orientation is currently under study.

The activation parameters measured by surges following step stress changes in transient creep experiments between 77°K. and room temperature have established that the activation area is strongly stress dependent and suggests the presence of a substantial effective internal stress which is likely due to thermally impenetrable forest dislocations. Considerable scatter in the activation area in the same crystal under identical step stress changes suggests irregularities in the obstacle structure are not completely averaged out in the small plastic strain surges.

2.0 Dislocation Dynamics

Further theoretical considerations of dislocation motion through thermally penetrable random obstacles have established that although considerable sideways unzipping occurs in the forward motion of the dislocation after its release from overstressed key obstacles, the total forward motion time is only slightly shorter than the activation time of the average obstacle. When obstacles are flexible such as forest dislocations, they are plucked during intersection by being swept forward by primary dislocations. This increases the steady state obstacle density along the dislocation considerably, delays athermal break through, and can result in an unusually low activation distance. Evidence for these theoretical studies has been found in dislocation displacement measurements in pure Na Cl crystals under stress pulses.

The consideration of mobile dislocation interactions in a crystal with lattice drag has resulted in a simple theory for the stress dependence of the mobile dislocation density in the absence of any other stationary obstacles. It is found that in this limiting case the mobile dislocation density cannot have a stress dependence larger than a power of two. If the difference in the stress exponents between the strain rate and the dislocation velocity is larger than two, this must be due to an effective internal stress.

3.0 *Plasticity in Polymers

Single crystals of high purity polyethylene having a small spread of molecular weight were deposited on copper single crystals, subjected to intense shear through the slip bands of the substrate copper crystals and studied by high resolution electron microscopy. The results show that at room temperature the polyethylene crystals can accommodate to any substrate shear whether in their plane or out of their plane. At 77°K., however, the crystals can accommodate only random out-of-plane shears and seem to be resistant to in-plane shears. Further such experiments at lower temperature are planned to determine the role of intra-lamellar dislocations in the

plastic deformation of crystalline polymers.

Publications:

A. S. Argon, "Interaction of Mobile Dislocations", submitted to Scripta Metallurgica.

A. S. Argon, "Motion of Dislocations through Thermally Penetrable Random Obstacles", in preparation.

A. S. Argon and G. E. Padawer, "Plastic Deformation in Pure Na Cl Crystals", in preparation.

II. MECHANISMS OF FATIGUE DAMAGE IN SEMI-BRITTLE MATERIALS AT ELEVATED TEMPERATURE AND FATIGUE IN COMPOSITES

Faculty:

*A. S. Argon, Professor, Mechanical Engineering

Research Staff:

R. Safoglu, Visiting Engineer, Mechanical Engineering

Graduate Students:

*I. Choi, Research Assistant, Mechanical Engineering

*D. H. Hunt, Research Assistant, Mechanical Engineering

*R. Scanlan, Undergraduate Assistant, Mechanical Engineering

*D. Bailey, Undergraduate Assistant, Mechanical Engineering

Support Staff:

W. Henry, Instrument Maker, Mechanical Engineering

R. Graudins, Secretary, Mechanical Engineering

Personnel who have left:

D. H. Hunt (now graduate student, Mechanical Engineering)

R. Scanlan (now graduate student, Mechanical Engineering)

Degrees Granted:

D. H. Hunt, S.M. Mechanical Engineering, June 1970

Sponsorship:

*Advanced Research Projects Agency, SD-90 DSR 75109

Research Report

1.0 Fatigue Damage in High Melting Point Semi-Brittle Materials at Elevated Temperatures

Technical difficulties with a high temperature vacuum chamber for the SF-2 fatigue machine have been overcome. The machine which has a low thermal inertia heating system is capable of a high specimen cooling rate ($\sim 100°C.\ sec^{-1}$) which is limited only by the rate of radiant heat transfer from the hot specimen to the cold walls of the vacuum chamber. Prior to the

investigation of the elevated temperature fatigue in Mg O and $Al_2 O_3$ the machine is presently used to determine the kinetics of the development of fatigue porosity in LiF. Preliminary experiments have established that there are strong similarities between the development of fatigue porosity by vacancy coalescence and porosity development by neutron irradiation at elevated temperature. In both instances, for similar vacancy production rates, the rate of development of porosity is maximum at a certain fraction of the absolute temperature (~ 0.6 Tm) and falls off sharpely on both sides. The experiments currently conducted are based on precision measurement of density in LiF as a function of the number of fatigue cycles.

Similar experiments to the ones described above for LiF are also being carried out on Fe-3% Si both in single and polycrystalline form. The density changes are being measured by quantitative metallography of pores on cleavage surfaces of partially fatigued specimens.

2.0 Fatigue in Laminates

Laminates of soldered steel sheets with transverse cracks were fatigued as a model of fatigue in laminates. Because of uncontrollable oxidation in the solder, the results were subject to large scatter in fatigue life. Examination of the fracture surfaces showed that fatigue is by cyclic delamination bridging the initially introduced transverse cracks.

Experiments are now in progress on transparent laminates of ribbon glass and polyethylene. The initial flaw distribution in the ribbon glass is such that in tension-release experiments some stable fragmentation should occur in the ribbon glass under the first application of the peak tensile stress per cycle, this should then be followed by cyclic delamination in response to the fatigue stress range per cycle.

Theses:

D. H. Hunt, "Crack Propagation During Fatigue of a Composite Material", S.M. Thesis, Mechanical Engineering, June 1970

Publications:

R. N. Wright, and A. S. Argon, "Fatigue Crack Propagation in Silicon Iron", Metallurgical Trans., in the press.

III MECHANICS AND PHYSICS OF DAMAGE IN COMPOSITE MATERIALS

Faculty:

* C. A. Berg, Associate Professor, Mechanical Engineering

Graduate Students:

D. Hiatt, Research Assistant, Mechanical Engineering

V. Agarwal, Research Assistant, Aeronautical Engineering

Support Staff:

* W. Henry, Instrument Maker, Mechanical Engineering
* Robin Schneider, Secretary, Mechanical Engineering

Personnel who have left:

D. Hiatt, now en route to US Department of Transportation

Degrees Granted:

D. Hiatt, MS and BS, Mechanical Engineering September 1970.

Sponsorship:

* Advanced Research Projects Agency, SD-90, DSR 75110

Research Report

1.0 Progress

1.1 Fracture

D. Hiatt has completed an experimental study of fracture extension from a pre-existing notch tip in a fiber reinforced resin composite. His results show (1) that under quasistatic loading fracture always extends parallel to the fiber direction with no fibers being broken, and (2) that the notch tip opening displacement is, at first, linear with load on the specimen, and then after reaching a critical value increases as the square of the load, as one expects from classical fracture mechanics. Hiatt's findings shed considerable light on the nature of local deformation prior to fracture extension.

1.2 Fatigue

M. Salama, under joint support of the Center for Material Science and Engineering and Celanese Corporation has discovered that cyclic compression causes crack extension transverse to the fiber direction of a unidirectional fiber composite, and that this fatigue process shows coaxing in a very pronounced way. Mr. Salama is now investigating the correlations between observed fatigue crack extension rates and the parameters (e.g., stress intensity factor, plastic zone radius) which determine the local stress field at the tip of the crack. The fatigue damage mechanism, in Mr. Salama's experiments, is microbuckling of the fibers at the notch tip, and his findings indicate that cyclic compression is the most serious condition to consider in design of composite structures.

1.3 Fracture of Laminates

V. Agarwal, working under joint support of the Center for Materials Science and Engineering and the Celanese Corporation, has used cine-microphotography to investigate tensile extension of pre-existing cracks in balanced fiber reinforced composite laminates. His observations show that gross crack extension takes place by progressive cracking parallel to the fiber direction in each lamella, until a sufficiently high load has been thrown onto the fibers of those plies aligned with the tensile axis, to cause transfibrile fracture. Once transfibrile fracture has occurred the process of interfibrile fracture starts again and the process is repeated. The essential point to come out of these observations is that interfibrile cracking of individual plies, supported by the interlaminar shearing of the resin used to cement the laminate, is the key process in fracture extension. Theoretical studies of the nature of the stress and strain singularity about the tip of such a crack are being undertaken so that a modified form of fracture mechanics to describe this process can be posed.

1.4 Wear

Preliminary studies of friction and wear of graphite fiber reinforced composites have indicated that low modulus ($E \sim 35 \times 10^6$ psi) graphite fibers show exceptionally high resistance to wear; wear coefficients of 10^{-7} at a load of 2Kg were measured. The potential of this material for use in wear resistant parts is under continuing study.

Publications, Theses and Reports:

C. A. Berg, R. Melton, T. Dunn, and I. Kalnin, "An Experimental Study of Fracture in the Grip Section of a Tensile Specimen," to appear Journal of Materials, 1970.

D. Hiatt, "Fracture of Prenotched Unidirectional Glass Fiber Reinforced Composites, MS Thesis, Mechanical Engineering Department, Massachusetts Institute of Technology, September 1970.

IV. SURFACE PROPERTIES AND PROCESSES

Faculty:

R. E. Stickney, Associate Professor, Mechanical Engineering

Research Staff:

Dr. T. Krivachy, DSR Staff, Mechanical Engineering

P. C. Abbott, Engineering Assistant, Mechanical Engineering

Graduate Students:

V. S. Aramati, Graduate Student, Mechanical Engineering

T. L. Bradley, Graduate Student, Mechanical Engineering

A. E. Dabiri, Research Assistant, Mechanical Engineering

T. E. Kenney, Research Assistant, Mechanical Engineering

C. N. Lu, Graduate Student, Mechanical Engineering

D. V. Tendulkar, Research Assistant, Mechanical Engineering

Support Staff:

Madeleine Leullier, Secretary, Mechanical Engineering

Personnel who have left:

Dr. T. Krivachy (Now seeking employment in Austria)

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 72256 and DSR 72290

Joint Services Electronics Program, DA28-043-02536(E), DSR 72561

National Aeronautics and Space Agency, NGL 22-091, DSR 76127

Petroleum Research Fund, DSR 29188

Sylvania Electric Corp., DSR 72426

Research Report

1.0 Heterogeneous Reactions at Gas-Solid Interfaces

Personnel: R. E. Stickney, T. Krivachy, A. E. Dabiri, T. L. Bradley, T. E. Kenney

Sponsorship: Advanced Research Projects Agency, Petroleum Research Fund

We have modified an existing molecular beam apparatus to make it suitable for studying heterogeneous catalytic and oxidation reactions. At present

we are observing the scattering of He atoms from a tungsten crystal that has been exposed to oxygen in a controlled manner. Preliminary results show that the He scattering pattern is extremely sensitive to the presence of oxygen on the tungsten surface.

2.0 Surface Examination Techniques

Personnel: R. E. Stickney and V. S. Aramati

Sponsorship: Advanced Research Projects Agency

Upon the departure of D. P. Shoemaker, R. E. Stickney became supervisor of the center facility for surface examination by low-energy electron diffraction (LEED) and by Auger electron spectroscopy. The existing LEED apparatus has been modified to include the Auger technique, and a second Auger apparatus having far greater sensitivity is being developed.

3.0 Gas-Solid Interactions

Personnel: R. E. Stickney, D. V. Tendulkar, A. E. Dabiri, T. E. Kenney

Sponsorship: Joint Services Electronics Program

Measurements of the spatial distribution of hydrogen molecules desorbed from polycrystalline and single-crystal nickel surfaces show that the distribution is concentrated in the direction of the surface normal to greater degree than predicted by the common assumption of diffuse emission. We also have measured the speed distribution of molecules desorbed in the normal direction, and the results correspond closely to the distribution of an equilibrium gas at the temperature of the nickel sample. We are attempting to develop a satisfactory explanation of the mechanism responsible for the non-diffuse spatial distributions.

4.0 Surface Properties of Thermionic Electrodes

Personnel: R. E. Stickney, V. S. Aramati

Sponsorship: NASA

Modulated beam techniques were employed to determine the binding energy of cesium on (100) and (110) single-crystal tungsten surfaces. These data, together with our previous measurements of the work function of the cesium-tungsten system, provide a rather complete description of the adsorption state. We also have completed an analysis of the rate of erosion of tungsten by oxidation at high temperature and low pressure. Work continues on the development of an Auger electron spectrometer for determining the chemical composition of surfaces.

5.0 Chemical Reactions in Lasers

Personnel: R. E. Stickney, C. N. Lu, P. C. Abbott

Sponsorship: Sylvania Electric Corp.

During the past year we have initiated an experimental and analytical investigation of the chemical reactions of oxygen and halogen gases with solid tungsten. Our objective is to obtain an accurate description of the metal transport reactions occurring in halogen-tungsten arc and incandescent lamps.

Publications:

J. C. Batty and R. E. Stickney, "Quasiequilibrium Treatment of Gas-Solid Reactions. I. Evaporation Rates of Volatile Species Formed in the Reaction of O_2 with W, Mo, and C", J. Chem. Phys. 51, 4475 (1969).

J. C. Batty and R. E. Stickney, "Quasiequilibrium Treatment of Gas-Solid Reactions. II. Flash Desorption of Oxidation Products from a Tungsten Surface", J. Chem. Phys. 51, 4485 (1969).

D. L. Fehrs, T. J. Lee, B. J. Hopkins, and R. E. Stickney, "Comments on 'An Electron Diffraction Study of Cesium Adsorption on Tungsten'", Surface Sci. 21, 197 (1970).

R. E. Stickney, "Review of the Interaction of Neutral Molecules with Solid Surfaces", J. Vac. Sci. and Technol. 7, 90 (1970).

D. L. Fehrs and R. E. Stickney, "Contact Potential Measurements of the Adsorption of Alkali Metals on Ta(110) and W(100) Crystals", Surface Sci. (in press).

A. E. Dabiri, T. J. Lee, and R. E. Stickney, "Spatial and Speed Distributions of H_2 and D_2 Desorbed from a Polycrystalline Nickel Surface", Surface Sci. (in press).

V STRUCTURAL MATERIALS

Faculty:

* F. J. McGarry, Professor, Civil Engineering
R. C. Jones, Associate Professor, Civil Engineering
F. Moavenzadeh, Associate Professor, Civil Engineering
* S. P. Shah, Visiting Associate Professor, Civil Engineering
J. F. Elliott, Visiting Assistant Professor, Civil Engineering
J. N. Sultan, Assistant Professor, Civil Engineering

Research Staff:

* O. E. Gjorv, Research Associate, Civil Engineering
J. E. Soussou, Research Associate, Civil Engineering
J. T. King, Technical Instructor, Civil Engineering
A. J. O'Neill, Technical Instructor, Civil Engineering
D. J. Hughes, Research Engineer, Civil Engineering
M. J. Markow, Research Engineer, Civil Engineering
R. W. Pratt, Research Engineer, Civil Engineering

Graduate Students:

J. A. Alexander, Research Assistant, Civil Engineering
R. J. Dauksys, Graduate Student, Civil Engineering
M. J. Doyle, Research Assistant, Civil Engineering
H. K. Findakly, Research Assistant, Civil Engineering
* P. Forootan-Rad, Research Assistant, Civil Engineering
S. A. Frondistou-Yannas, Research Assistant, Civil Engineering
R. C. Laible, Graduate Student, Civil Engineering
T. J. Lamb, Research Assistant, Civil Engineering
A. C. Lemer, Teaching Assistant, Civil Engineering
J. F. Mandell, Research Assistant, Civil Engineering
A. Naaman, Research Assistant, Civil Engineering
E. F. Olster, Research Assistant, Civil Engineering
C. V. Ramos-Roya, Graduate Student, Civil Engineering

Support Staff:

A. P. Rudolph, Jr., Machinist, Civil Engineering
R. E. Boyd, Administrative Assistant, Civil Engineering
Maria E. Fleites, Language Assistant, Civil Engineering

Rosemary H. Driscoll, Secretary, Civil Engineering
Lenore Kistler, Secretary, Civil Engineering
Barbara Lynn, Secretary, Civil Engineering
Maureen A. Mack, Secretary, Civil Engineering
Martha E. McGarry, Secretary, Civil Engineering
Janet H. Neale, Secretary, Civil Engineering

Degrees Granted:

J. A. Alexander, Ph.D., Civil Engineering, September 1970
R. J. Dauksys, S.M., Civil Engineering, June 1970
P. Forootan-Rad, Ph.D., Civil Engineering, June 1970
S. A. Frondistou-Yannas, S.M., Civil Engineering, June 1970
R. C. Laible, Ph.D., Civil Engineering, June 1970
A. Naaman, S.M., Civil Engineering, September 1970
C. V. Ramos-Royo, S.M., Civil Engineering, September 1970
J. E. Soussou, Ph.D., Civil Engineering, June 1970

Research Report

1.0 The Relationship Between Microstructure and Mechanical Properties of Cementitious Materials

Personnel: F. J. McGarry, S. P. Shah; O. E. Gjorv, A. Naaman, C. V. Ramos-Royo, S. A. Yannas

Sponsorship: Advanced Research Projects Agency, SD-90, DSR 78898

1.1 Environmental Fatigue of Concrete

The performance of paste, mortar and concrete subjected to repeated wetting and drying in plain water and in sodium and sulphate solutions, and freezing and thawing, was investigated. The methods used to examine deterioration included: changes in weight and length, changes in flexural strength, changes in time of travel for ultrasonic pulses, quantitative and qualitative optical microscopy, scanning electron microscopy and energy dispersive x-ray analysis. The results showed that the amount and sizes of aggregate may be as important for durability as is the

water-cement ratio. Small size aggregates appeared to retard fracture better than larger ones, apparently because of their effect on the size of matrix cracks. The extent of corrosion was best reflected by the measurements of pulse time and micro-cracking. Measurements of length were not always reliable while those of weight did not consistently indicate damage.

1.2 Ferro-Cement

Engineers have long searched for materials for construction of shells which are strong as well as light, since the advantages of shell construction are increased by using materials of large strength-weight ratio. One such material appears to be ferro-cement (wire-mesh reinforced mortar). Since Nervi built ferro-cement shells in the form of boat hulls and building roofs, there has been increasing interest in this type of construction. In spite of growing popularity, very little information on which a rational design may be based is available. Lack of such information makes evaluation and possible uses of this material difficult. The purpose of this research was to study elastic, cracking, and ultimate behavior of ferro-cement. To compare ferro-cement with conventional reinforced concrete, the influence of volume of steel, type of mesh, and mesh dimensions were investigated.

From experimental findings it was concluded that the relatively large specific surface area of reinforcement, about one order higher than that for conventional reinforced concrete, makes possible more efficient use of both concrete and steel. The improved bond between steel and the matrix and the presence of transverse reinforcement result in very fine numerous micro-cracks, a performance which Nervi called "crack free." It was possible to predict cracking behavior of ferro-cement by extending existing theories of cracking for conventional reinforced concrete. The properties of mesh, such as its shape, method of weaving, the direction of weaving with respect to that of testing, and its ductility significantly influenced the tensile

behavior of ferro-cement. Using theories of composite materials, it was possible to predict the elastic and the ultimate behavior of ferro-cement.

The possibility of obtaining high tensile strength (up to 4000 psi) with a relatively small width of cracks (.002") and other advantages inherent to conventional reinforced concrete makes ferro-cement a material to consider for construction of thin shells, boats, and containment vessels such as tanks for storing liquid gases.

1.3 Lightweight Concrete

For normal weight concrete, the water-cement ratio is the primary factor influencing strength. In contrast, for lightweight concrete, in addition to the water-cement ratio, the volume fraction of lightweight aggregates is also critical for determining strength. As a result, for a given strength of lightweight concrete, it is possible to obtain several mix proportions by modifying the volume fraction of aggregates and by changing the water-cement ratio. Optimum mix proportions depend upon the relative values of strength-weight and strength-cost ratios. The design for optimum mix proportions depends in part on satisfactory prediction of the relation between strength of concrete and volume fraction of lightweight aggregates.

In tnis research, several experimental and analytic methods of determining strength of lightweight aggregates were studied. Two types of aggregate were employed. Confined compression tests on groups of particles of varying sizes were made. In addition, single particles were subjected to direct tensile tests and shear compression tests. These test results indicated that although none of these tests can directly predict the contribution of aggregates to the strength of concrete, they can be useful for quality control as well as for verification of a suitable analytic approach.

To determine the relations among the strength of concrete and those of aggregates and mortar matrix, concrete specimens were

tested in compression and in split cylinder mode at several ages of curing. Measurements of strains and of quantities of fractured aggregate particles were made during a total of 150 tests. Based on experimental findings and on theories of composite materials, an analytic model was developed. This model permits quantitative evaluation of the contribution of aggregates to the strength of concrete as a function of the volume fraction of the aggregates, the strength of the concrete, and the strength of the corresponding mortar matrix.

Strength of any given type of lightweight aggregate can be determined from the compression tests of concrete and of corresponding mortar with this method. Based on knowledge of the strength of given aggregates, optimum design is possible.

1.4 Polymer Modified Concrete

To explore the possible uses of polymer latex modified portland cement mortar and to understand the mechanism of their modification, physical, chemical, mechanical and durability properties of latex films and of modified and unmodified mortars were studied. Two polyvinyl acetate copolymers and one styrene butadiene copolymer and emulsion were investigated. Significant improvements in extensibility and some durability properties were obtained with latex modification. Modified mortars formed a strong bond with porous material, such as old concrete through mechanical interpenetration. Superior bond strength and toughness, necessity of dry curing and economic considerations suggest that modified mortars may advantageously be employed for surface treatments such as coatings and sealants. Higher volume changes during wetting and drying, lower modulus of elasticity and lower compressive strength were observed for modified mortars. Although continuous wet curing reduces the strength of modified mortars, subsequent drying increases their strengths. For PVA modified mortars, this was partly explained by the performance of latex films in saturated lime solutions.

Related Academic Subjects

1.40 Introduction to Electron Microscopy

1.44 Cementitious Materials

1.46 Portland Cement Concrete

Theses:

S. A. Frondistou-Yannas, "Mechanical Properties of Cement Mortars Modified by Polymers," S.M., Civil Engineering, M.I.T., June 1970.

A. E. Naaman, "Reinforcing Mechanisms in Ferro-Cement," S.M., Civil Engineering, M.I.T., September 1970.

C. V. Ramos-Royo, "Strength of Lightweight Aggregate," S.M., Civil Engineering, M.I.T., September 1970.

Publications:

O. E. Gjorv and S. P. Shah, "Concrete Subjected to Environmental Fatigue," Publication R70-42, Civil Engineering, MIT, July 1970.

S. A. Frondistou-Yannas and S. P. Shah, "Polymer Latex Modified Mortar," Publication R70-45, Civil Engineering, MIT, July 1970.

S. P. Shah and R. V. Rangan, "Some Micromechanical Properties of Fiber Reinforced Concrete," Publication R69-72, Civil Engineering, MIT, December 1969.

VI. HETEROGENEOUS CATALYSIS

Faculty:

R.F. Baddour, Professor, Chemical Engineering
M. Modell, Assistant Professor, Chemical Engineering

Graduate Students:

J.I. Apse, Graduate Student, Chemical Engineering
H.D. Cochran, Graduate Student, Chemical Engineering
R.J. Donnelly, Graduate Student, Chemical Engineering
J.B.L. Harkness, Graduate Student, Chemical Engineering
K.J. McNulty, Graduate Student, Chemical Engineering

Support Staff:

E.J. Denning, Secretary, Chemical Engineering
S.R. Mitchell, Technical Instructor, Chemical Engineering

Personnel who have left:

J. Aleksandrowicz, Research Assistant, Chemical Engineering (Now at Companhia Quimica Industrial de Laminados, Rio de Janeiro, Brazil).
R.A. Sills, Research Assistant, Chemical Engineering (Now at American Cyanamid Research Division).

Degrees Granted:

J. Aleksandrowicz, Ph.D., Chemical Engineering, June, 1970.
R.A. Sills, Ph.D., Chemical Engineering, June, 1970.

Sponsorship:

National Science Foundation GK-1699X. DSR 71895

Research Report

One of the long-term objectives of this program is to develop methods for evaluating specific rate constants of elementary catalytic reactions. It is believed that these specific rate constants will be more amenable than overall rate constants to meaningful correlation with parameters of the catalyst. To evaluate specific rate constants, it is necessary and sufficient

to know the true sequence of elementary steps (i.e., the mechanism), the rate of the overall reaction, and the concentrations of surface intermediates.

The near-term objectives are to develop techniques for determining mechanisms and concentrations of surface intermediates. To date, efforts have been concentrated on metal-catalyzed, gas-phase reactions.

One method proposed for determining mechanisms and surface concentrations consists of using infrared spectroscopy to measure surface conditions. Surface spectra and overall rate are followed at various temperatures and gas compositions. Postulated mechanisms are tested directly by comparing experimental and theoretical forms of the rate expressed in terms of surface concentrations.

In an experimental program initiated in 1963, simultaneous infrared transmission and kinetic measurements were made for CO oxidation on silica-supported palladium catalysts. For the CO-Pd system, two types of surface species were identified by infrared spectroscopy. Palladium-oxygen absorption bands were not observed because the background absorption of the silica support is intense in the region where Pd-O_2 bands are believed to occur. The results indicated clearly the inadequacy of the conventional kinetic approach and the value of simultaneous measurements. However, the experiments were not sufficient to identify unequivocally the reaction mechanism because precise values of surface concentrations were hampered by the coexistence of several forms of adsorbed CO.

Recently, preliminary experiments were made in an attempt to apply this technique to CO oxidation on platinum. It was believed that the extinction coefficient for the Pt-CO system would be easier to obtain than that for the Pd-CO system because the former system contains only one infrared band, and thus, it had been proposed that only one CO surface species existed on Pt. However, measured extinction and adsorption isobars exhibit maxima and minima which are indicative of at least two distinct surface species having the same C-O stretching frequency. Furthermore, the presence of oxygen in the gas phase alters the spectrum of adsorbed CO. Consequently, effective extinction coefficients of adsorbed CO must be determined during simultaneous adsorption of O_2 if surface spectra are to be related to surface

concentrations under reaction conditions. Such experiments are currently in progress.

A second set of experiments has been conducted with the aim of developing general techniques for observing infrared absorption bands of all surface species. The conventional infrared method involves transmissions spectroscopy in which small particles of metal (50 Å) are supported on finely divided silica or alumina (100 Å). Large regions of the infrared are obscured by the intense absorption of these supports. Thus, metal-oxygen and metal-carbon bonds have not been observed because they are believed to occur in the region of the silica continuum. Determination of the latter would be unequivocal evidence for or against coexistence of two forms of adsorbed CO having the same C-O stretching frequency. In an effort to surmount the limitations of conventional transmission spectroscopy, an attempt was made to observe reflection spectra of unsupported metals. An interferometer was used to measure the relatively weak signals. From a theoretical analysis of the reflection process, it was estimated that with 40 to 60 reflections of the infrared beam between metal foils, it should be possible to quantitatively measure concentrations of surface species down to 1% of a monolayer in the range of 250 to 3500 cm^{-1}.

The reflection technique has been successively employed for CO adsorption on palladium foils. Fundamental vibrations of carbon-oxygen stretching, palladium-carbon stretching, and palladium-carbon-oxygen bending have been observed at 435, 475, and 2042 cm^{-1}. The results also indicate that reflection spectra can be obtained much more readily than as predicted by theoretical analysis. We believe that these results represent a technological break-through; the reflection technique will permit direct observation of phenomena which have been the subject of much speculation and conjecture.

The reactions studied to date (CO oxidation on supported Pt and Pd) are more complicated than anticipated initially and presently available techniques are not yet sophisticated enough to handle these complex reactions. Therefore two other programs were initiated to study what are believed to be simpler reactions: one is concerned with $H_2 - D_2$ exchange on polycrystalline nickel, and the other is concerned with the rates of adsorption and desorption of CO and NO on a number of transition metals. Both

of these projects is described below.

Although H_2 - D_2 exchange on metals (and on nickel in particular) has been the subject of numerous studies, the mechanism is far from understood. Several mechanisms have been proposed, but each is unduly naive because only one form of adsorbed hydrogen is considered to be present (molecular in the Rideal-Eley mechanism, atomic in the Bonhoeffer-Farkas mechanism, etc.). Within the last twenty years, new techniques have been used (*e.g.*, infrared, flash desorption, work function) to show that many adsorbed forms of hydrogen coexist on a given metal, the number of forms increasing with increasing pressure.

The third investigation was initiated in 1968 to determine the mechanism of H_2 - D_2 exchange taking account of the multiple forms of adsorbed hydrogen. The approach once again is to determine simultaneously overall rates and concentrations of individual adsorbed species. Temperature-programmed desorption is to be used to determine surface concentrations of adsorbed species.

The fourth experiment, initiated in 1968, was directed at studying the rates of an even simpler system. The behavior of CO and NO during chemisorption on a series of clean transition metal films will be investigated. The temperature-programmed desorption technique will be utilized to identify the various species chemisorbing at room temperature and at pressures from 10^{-9} to 10^{-2} torr. The rate of adsorption of the various surface species will be determined by varying the time of adsorption prior to the temperature-programmed desorption. The data will be analyzed in terms of the rate expressions of each of elementary steps involved in the chemisorption-desorption process. It is further suggested that infrared spectra of the covered metal surfaces obtained by a multiple-reflection technique will yield information on the structure of the various species chemisorbed. The feasibility of applying such a technique in an experimental system in which temperature-programmed desorption studies can also be carried out will be investigated. The ultimate goal of this project is to increase our understanding of the elementary steps involved in the formation of multiple types of adsorbed species, and to develop correlations of the specific rate constants for the chemisorption processes with parameters of the catalyst.

In an unrelated vein, an exploratory program has recently been completed on the effect of visible and ultraviolet light on gas-phase, metal-catalyzed reactions. In earlier studies, it was demonstrated that light has an appreciable effect on the rate of carbon monoxide oxidation over a palladium catalyst. The effect was attributed to electronic excitation of a surface-adsorbate bond which, in turn, results in a change in the rate of desorption of surface species. The objectives of the recent study was to determine the extent to which other systems can be similarly affected, and to investigate more thoroughly the mechanism of the photocatalysis. It was shown that the hydrogenation of ethylene on platinum foil is sensitive to near UV irradiation. Light in the range of 2600 to 3600 Å had a significant inhibiting effect on the rate of the catalyzed hydrogenation. It is believed that irradiation results in photochemical desorption of adsorbed ethylene and the decrease in rate occurs because surface reaction of ethylene and hydrogen is the rate-limiting step.

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R.A. Sills, "Simultaneous Infrared and Kinetic Studies of Platinum Catalyzed Carbon Monoxide Oxidation," Ph.D., Department of Chemical Engineering, June, 1970.

Publications:

R.F. Baddour, M. Modell, and R.L. Goldsmith, "The Palladium-Catalyzed Carbon Monoxide Oxidation. Catalyst "Break-in" Phenomenon," J. Phys. Chem., 74, 1787 (1970).

R.F. Baddour and M. Modell, "The Effect of Visible and Ultraviolet Light on the Palladium-Catalyzed Oxidation of Carbon Monoxide," J. Phys. Chem., 74, 1392 (1970).

VII MOLECULAR BEAM DETECTOR - ADSORBATE SPUTTERING

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Sponsorship:

Air Force Office of Scientific Research, AF 49(638)-1601, DSR 76043

* Advanced Research Project Agency, SD-90, DSR 71628, 72257, DSR 78880, 72283

Research Report

We are attempting to detect a molecular beam of neutral krypton with translational energies of a few electron volts or larger by the process of collisional sputtering of an alkali metal adsorbed at low coverage on a metal surface. Since the alkali metal is sputtered as ions from a variety of metal surfaces, the process should provide a direct electrical signal propertional to the intensity of the incoming krypton beam.

1.0 Thermal Desorption

Personnel: J. P. Moran, L. T. Ong

Sponsorship: Advanced Research Projects Agency

The fabrication of the detector is completed and an initial study of the removal of adsorbed alkali metal ions by thermal desorption is in progress. Control of this conventional method for ion adsorbate removal is essential before we can proceed to the untried method of removal by sputtering. A favorable comparison of ion desorption rate versus alkali metal vapor pressure with results of previous investigations will indicate that the chemical composition of our substrate surface is suitable for the subsequent adsorbate sputtering studies.

2.0 Molecular Beam

Personnel: J. P. Moran, L. T. Ong, P. H. Bauer

Sponsorship: Advanced Research Project Agency, Air Force Office of Scientific Research

A molecular beam source capable of producing nearly monoenergetic beams of heavy gases with energies up to several electron volts has been constructed. A study of beam intensity and energy as a function of source temperature, gas supply pressure and composition and source geometry is underway.

3.0 Ion Adsorbate Sputtering

Personnel: J. P. Moran, L. T. Ong

Sponsorship: Advanced Research Project Agency

A coarse theoretical analysis of adsorbate sputtering and a review of available data on bulk phase sputtering by neutral particles leads us to believe that the proposed molecular beam detection scheme will provide adequate sensitivity to conduct a parametric study . This study will follow completion of those discussed in (1.0) and (2.0) above.

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